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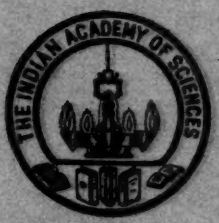
VOL. XLIV] *SECTION A* [No. 3

SEPTEMBER 1956

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# THE DIAMOND*

By Sir C. V. Raman

(*Memoir No. 86 from the Raman Research Institute, Bangalore-6*)

Received September 5, 1956

## 1. Introduction

The many remarkable properties which diamond exhibits, taken in conjunction with the simplicity of its crystal structure and composition, make it a substance of quite exceptional interest to the physicist. In the hope that investigations made with it would result in significant contributions to knowledge, a collection of some five hundred diamonds was built up in the course of years and used by the present author and his collaborators in an extensive series of researches. It would not be possible in this lecture to survey all the topics investigated. We shall confine ourselves to the consideration of some results which have emerged from our studies and which are of fundamental significance for the physics of the solid state.

In his paper of 1907 introducing the quantum theory of specific heats, Einstein made use of the experimental data for the variation with temperature of the specific heat of diamond which had been discovered by earlier investigators to demonstrate the correctness of the basic ideas set out in his paper. The expression for the thermal energy of crystals as a function of temperature derived by Einstein in that paper was a logical deduction from his hypothesis that the structural units comprised in the crystal and capable of mechanical vibration obey the quantum rule, in other words, that their energy can only increase or diminish by quanta proportional to the frequency of vibration. Einstein did not however, deal with the question of how the modes and frequencies of vibration under consideration could be evaluated in the general case. In my address to the Lindau Conference this year, I showed how this basic problem can be handled rigorously and a solution obtained which reconciles the results of classical dynamics with the fundamental notions of the quantum theory and the principles of thermodynamics. Diamond is exceptionally well-suited for a test of the correctness of the theoretical approach set out in that address, since the necessary calculations are readily made and the experiments necessary to check the consequences of the theory are also feasible. It is the purpose of this lecture to show how perfectly the

* A lecture delivered at the Federal Polytechnic Institute in Zurich and at the Universities of Freiburg and Bonn early in July 1956, following the address on "The Physics of Crystals" given at Lindau in June, 1956. The latter address has been published in these *Proceedings* (Memoir No. 85 of the Institute), but the present memoir may be read independently of the same.

theory and the results of experiment are in accord with each other. For the sake of ready intelligibility, the subject will be dealt with from first principles.

## 2. THE CHARACTERISTIC VIBRATIONS OF LINEAR LATTICES

We shall commence by considering a few simple models of which the behaviour may serve to illustrate the principles underlying the general theory. The simplest of such models is a stretched string loaded by a series of equidistant particles of identical mass along its length. It is immediately obvious that a mode of oscillation is possible on such a string in which the successive particles have the same amplitude but opposite phases of vibration. Such an oscillation is pictured in Fig. 1 (*a*). It has all the characters of a normal mode of vibration and possesses a specific frequency which can therefore be regarded as characteristic of the system. We may next consider the case in which the particles on the string are equidistant but have alternately two different masses. It can be seen that such a system would have *three* possible modes of normal vibration with different frequencies. These modes are represented in Fig. 1 (*b*), (*c*) and (*d*) respectively. In Fig. 1 (*b*), successive particles of equal mass have identical amplitudes and oscillate in the same phase, while in Figs. 1 (*c*) and 1 (*d*), they have the same amplitudes but opposite phases, the situation thus being analogous to that pictured in Fig. 1 (*a*).

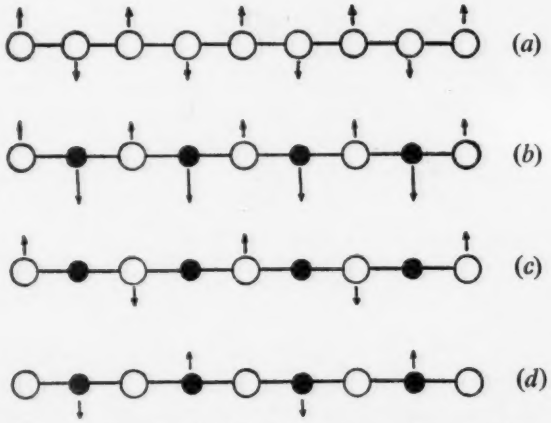


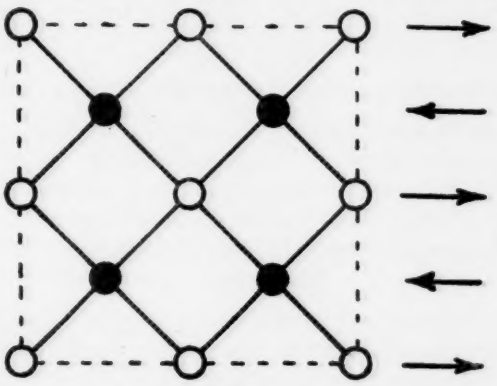

FIG. 1. The characteristic vibrations of linear lattices.

The foregoing results can readily be generalized. It can be proved that a periodic linear lattice with $p$ particles in each unit of its structure would have $(2p-1)$ normal modes and frequencies of vibration; in $(p-1)$ of these

modes, the amplitudes and phases of vibration of the corresponding particles in the successive units are the same, while in the $p$ other modes, they have the same amplitudes but opposite phases. It can also be shown analytically that any initial disturbance set up locally on such a linear lattice would resolve itself quickly into a summation of the $(2p-1)$ characteristic modes of oscillation with their respective frequencies.

### 3. The Normal Vibrations of Crystal Structures

The basic principle of crystal architecture is that its structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. It follows as a necessary consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should possess the same property. This can evidently happen in two ways, thereby enabling us to divide the normal modes in two distinct classes. In the first class of normal modes, the amplitudes as well as the phases of oscillation of the equivalent atoms which come into coincidence following an unit translation are identical. In the second class of normal modes, the amplitudes of equivalent atoms are the same but the phases are all reversed. Since these two alternatives are possible for a unit translation



Mode I.

Fig. 2. Diamond: the principal mode of oscillation.

along each of the three axes of the lattice, we have $2 \times 2 \times 2$ or 8 possible situations. In each of these situations, the equations of motion of the $p$ atoms contained in the unit cell of the structure can be written down and completely solved, giving us $3p$ solutions. Thus in all we have $24p$ solutions. $(3p-3)$ of these solutions represent normal modes of vibration of the first kind, $21p$ solutions represent normal modes of the second kind and the 3

remaining solutions represent the simple translations of the unit cell of the structure.

The general principles set forth above enable us to describe in simple geometric terms, the normal modes of vibration of the atoms located at the points of a Bravais lattice for each of the known fourteen species. In the general case when $p = 1$, we have 21 distinct normal modes and frequencies of vibration, besides the three translations. But, if the lattice possesses some elements of symmetry, the number of distinct frequencies would be notably reduced. We shall consider here the case of the face-centred cubic lattice. The primitive translations in such a lattice may be taken as the lines joining a cube corner with the centres of the three cube faces meeting at that corner. Applying the symmetry operations of the point group $O_h$ to which the lattice belongs and considering the 8 possible combinations of the phases of atomic vibration, the 21 modes of vibration which thereby result can be grouped together and described as follows: I: a vibration of the alternate octahedral planes of atoms with opposite phases normally to themselves (degeneracy 4); II: the same but transversely to the planes (degeneracy 8); III: the vibrations of the cubic planes of atoms normally to themselves (degeneracy 3); IV: the same but with the vibrations tangentially to the planes (degeneracy 6). The same results can be very simply deduced by inspection of a model exhibiting the unit rhombohedral cells in a face-centred cubic lattice.

## 4. THE VIBRATIONS OF THE DIAMOND STRUCTURE

The structure of diamond may be described as an interpenetration of two face-centred cubic lattices of carbon atoms, each atom in one lattice being linked to its four nearest neighbours in the other lattice by tetrahedrally directed valence bonds. This situation is diagrammatically represented in Fig. 2 by a projection of the cubic cell on a plane normal to the cubic axis. (No attempt is made to show the different planes in which the atoms lie.)

The normal modes of vibration of the atoms in the diamond structure may be very simply derived from those for a simple face-centred lattice listed above by taking into account the phases of the motion of the atoms in the two lattices which may be either the same or opposite. The nine possible modes of vibration thus derived are depicted in Figs. 2, 3 and 4. The principal mode which is depicted in Fig. 2 is a translatory movement of the two lattices in opposite phases. This is triply degenerate and can occur along anyone of the three cubic axes, as indicated by the arrows in the figure. Fig. 3 shows the diamond structure viewed in a direction normal to a trigonal axis of symmetry and exhibits the octahedral layers of atoms. The normal and tangential movements of these planes in the two possible relative phases

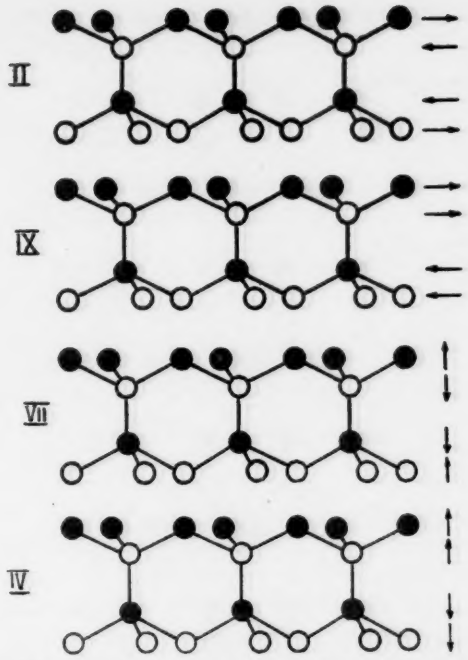



FIG. 3. Diamond: normal and tangential oscillations of the octahedral layers.

give us four modes of vibration; the directions of movement of the atomic planes are indicated by arrows in the figures. Fig. 4 shows the structure of diamond as viewed in a direction slightly inclined to a face diagonal and exhibits the cubic layers of atoms. The directions of movement of these layers in the four possible modes are likewise indicated by arrows in the figure.

Very simple considerations enable us to arrange the nine normal modes of vibration of the diamond structure in the descending order of their frequencies as indicated by the Roman numerals entered against them in Figs. 2, 3 and 4. The triply degenerate oscillation of the two interpenetrating lattices against each other shown in Fig. 2 would evidently have the highest frequency of all, since the movement involves variation of all the four bond lengths and all the six bond angles at each carbon atom; the restoring forces brought into play would therefore be the maximum possible. It is likewise evident that the mode marked IX in Fig. 3 would have the lowest frequency of all and the mode marked VIII in Fig. 4 would be the next lowest. For, in neither of these modes is there any variation of the bond lengths; in mode

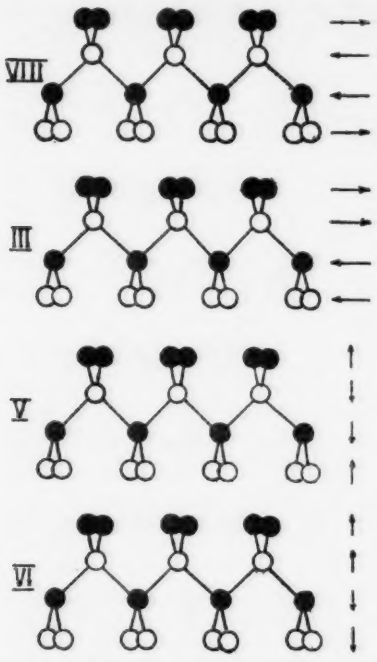



FIG. 4. Diamond: normal and tangential oscillations of the cubic layers.

IX, only two bond angles vary and in mode VII only four bond angles, the rest of them remaining unaltered. *Per contra*, the same modes but with the relative phases of motion of the adjacent layers reversed, *viz.*, mode II shown in Fig. 3 and mode III shown in Fig. 4 may be expected to have high frequencies which follow that of mode I in the order indicated. It remains to determine the sequence of the frequencies of the four remaining modes. It is obvious that the modes marked V and VI in Fig. 4 would have identical frequencies; for in these modes, the cubic layers which move normally to themselves, in other words along the cubic axis, are equidistant. Finally, we remark that the modes marked IV and VII in Fig. 3 may be expected to have frequencies respectively higher and lower than the common frequency of modes V and VI, though the differences would not be large. In mode IV, the oscillation involves the maximum stretching of one bond out of the four in the successive layers of the structure, the three others remaining invariable, while the mode VII, the bond along which the motion takes place remains of invariable length, while the three other bonds inclined at a large angle to the direction of movement are tilted periodically. The restoring forces

acting in the direction of movement may be expected to be distinctly greater in the former case than in the latter.

### 5. Numerical Evaluation of the Frequencies

Exact formulæ are readily derived for the eight distinct frequencies of vibration in terms of the force constants expressing the interactions between each carbon atom and the surrounding ones. The equations of motion from which these formulæ are derived take a very simple form by reason of the fact that the relative displacements of the atoms are either zero or else are twice the value of the absolute displacement of each atom. The force-constants are most conveniently defined in terms of the components of the relative displacements and the forces of interaction resolved along the three cubic axes and considering their ratios. The symmetry of the structure results in a very considerable diminution in the number of distinct force-constants: it is found that two constants express the interactions with the four nearest neighbours, five others the interactions with the twelve next nearest neighbours, and five more the interactions with the twelve more distant neighbours. However, on writing down the equations of motion, it emerges that only three of the five force-constants for the next nearest neighbours actually appear in them and that the five force-constants for the twelve more distant neighbours also appear in the equations as sums of which there are only two. Accordingly, if we restrict ourselves to the interactions with the twenty-eight nearest neighbours of any given atom, we have only seven force-constants to deal with.

The seven force-constants referrred to above will be denoted by $\alpha$, $\beta$ for the first four atoms; $\theta$, $\phi$, $\psi$ for the next twelve and $k$ and $\chi$ for the twelve atoms still further out. By way of explanation, it may be stated that the force-constant $\alpha$ refers to the case in which the force and displacement are both along the same cubic axis, while $\beta$ refers to the case in which they are mutually perpendicular. The constant $\theta$ refers to the case in which the force and displacement are parallel to each other but are both perpendicular to the line joining the atoms which is a face-diagonal of the cube; $\phi$ and $\psi$ refers to the cases in which the component forces and displacements both lie in the same plane as this diagonal, but the force and displacement are parallel to each other for $\phi$ and perpendicular for $\psi$. The constant $k$ refers to the cases in which the components of force and displacement are parallel to each other while $\chi$ refers to the cases in which they are mutually perpendicular. $k$ and $\chi$ both represent the joint effect of a whole set of twelve atoms.

Table I shows the eight frequencies of vibration arranged in the sequence already explained which will be found entered in the first column. The

TABLE I

*Evaluation of Frequencies*

| Mode No. | Degeneracy | Complete formula $4\pi^2\nu^2c^2m =$ | $\alpha, \beta$ only | $\alpha, \beta, \theta, \phi, \psi$ only | $\alpha, \beta, \theta, \phi, \psi, k, \chi$ |
|---|---|---|---|---|---|
| I | 3 | $4\alpha + 12k$ | 1332 | 1332 | 1332 |
| II | 8 | $3\alpha+\beta+2\theta+4\phi-2\psi+3k-3\chi$ | 1250 | 1285 | 1250 |
| III | 6 | $2\alpha+2\beta+4\theta+4\phi+6k+6\chi$ | 1162 | 1232 | 1239 |
| IV | 4 | $\alpha+2\beta+2\theta+4\phi+4\psi+9k-6\chi$ | 952 | 1099 | 1149 |
| V & VI | 3+3 | $2\alpha+8\phi+6k$ | 942 | 1088 | 1088 |
| VII | 4 | $3\alpha-2\beta+2\theta+4\phi+4\psi+3k+6\chi$ | 931 | 1068 | 1008 |
| VIII | 6 | $2\alpha-2\beta+4\theta+4\phi+6k-6\chi$ | 651 | 752 | 740 |
| IX | 8 | $\alpha-\beta+2\theta+4\phi-2\psi+9k+3\chi$ | 460 | 538 | 621 |

second column shows the degeneracy of each of these modes. The total of the figures shown in this column amounts to forty-five as is to be expected. The third column shows the operative force-constants in each case in terms of the seven force-constants, *viz.*, $\alpha$, $\beta$ for the first group; $\theta$, $\phi$, $\psi$ for the second group; $k$ and $\chi$ for the third group. In the fourth, fifth and sixth columns are given respectively the values of the frequencies calculated with only the first two constants, then with only five and finally with all the seven. The values of the constants in each case have been so chosen as to give the same frequency for the principal mode. They are given in Table II.

It will be remarked from Tables I and II that even with only two force-constants we obtain a rough approximation to all the frequencies and that with five constants we get a fair approximation to the values calculated with all seven constants shown in the last column of Table I. It will also be seen from Table II that the force-constants fall off rapidly in magnitude as we proceed to the more distant neighbours. The magnitudes of the force-constants in each group are also related to each other in the manner that could have been expected *a priori* from their respective definitions as given above.

TABLE II

*Values of Force-Constants Used*

| Force-constants | Table I, Column 4 | Table I, Column 5 | Table I, Column 6 |
|---|---|---|---|
| $\alpha$ | $3{\cdot}135\times10^5$ dynes/cm. | $3{\cdot}135\times10^5$ dynes/cm. | $2{\cdot}78\times10^5$ dynes/cm. |
| $\beta$ | $1{\cdot}637\times$ ,, | $1{\cdot}682\times$ ,, | $1{\cdot}746\times$ ,, |
| $\theta$ | .. | $0{\cdot}012\times$ ,, | $0{\cdot}010\times$ ,, |
| $\phi$ | .. | $0{\cdot}262\times$ ,, | $0{\cdot}262\times$ ,, |
| $\psi$ | .. | $0{\cdot}240\times$ ,, | $0{\cdot}228\times$ ,, |
| $k$ | .. | .. | $0{\cdot}12\times$ ,, |
| $\chi$ | .. | .. | $0{\cdot}00\times$ ,, |

## 6. THE SCATTERING OF LIGHT IN DIAMOND

Spectrograms of the light scattered by diamond when illuminated by the light of a mercury arc lamp exhibit, for each of the monochromatic radiations of the incident light, a single sharp line with a frequency shift of 1332 cm.$^{-1}$ which may be identified with the highest of the frequencies listed in Table I. But no lines appear with frequency shifts other than that mentioned. This is readily understood, since in all the modes except that of the highest frequency, the atomic oscillations have opposite phases in the successive layers, and hence the effects arising at these layers cancel each other out. Overtones and combinations of the frequencies of all the normal modes are, however, permitted to appear as frequency shifts in light scattering, thereby making the existence of these modes open to observation. That diamond would exhibit this type of light-scattering was theoretically predicted, following which experimental studies undertaken by Dr. R. S. Krishnan confirmed the expectations.

The second-order spectrum of light scattering is of extremely low intensity, and one has necessarily to use diamonds of small size for the experiments. Further, it is necessary to record the spectrum under high dispersion to enable its features to be adequately exhibited. These difficulties are successfully overcome by the aid of the extremely intense $\lambda$ 2537 radiations

emitted by a quartz water-cooled mercury arc when it is set between the poles of an electro-magnet. It is necessary, of course, to employ diamonds which are transparent to the ultra-violet region of the spectrum. In these circumstances, it is also essential to use mercury vapour as a filter inside the spectrograph to absorb the intense λ 2537 radiations before they reach the photographic plate, and thus prevent its fogging.

Spectrograms obtained in the manner explained are reproduced as Fig. 1 in Plates II and III respectively. The spectrum in Plate II was recorded with a medium-sized spectrograph and that in Plate III with a larger instrument of higher resolving power. A microphotometer record of the spectrum obtained with the smaller instrument is reproduced in juxtaposition with the spectrum itself as Fig. 2 in Plate II, below which has been placed the spectrum of the mercury arc alone as a comparison. Fig. 2 in Plate III reproduces the microphotometer record of the second-order spectrum obtained with the larger instrument and below it the spectrum itself to admit of ready comparison with the features seen in it.

The features visually observed in the spectra and confirmed by inspection of their microphotometric records are diagrammatically represented in Fig. 5 below, the measured frequency shift being indicated against each feature.

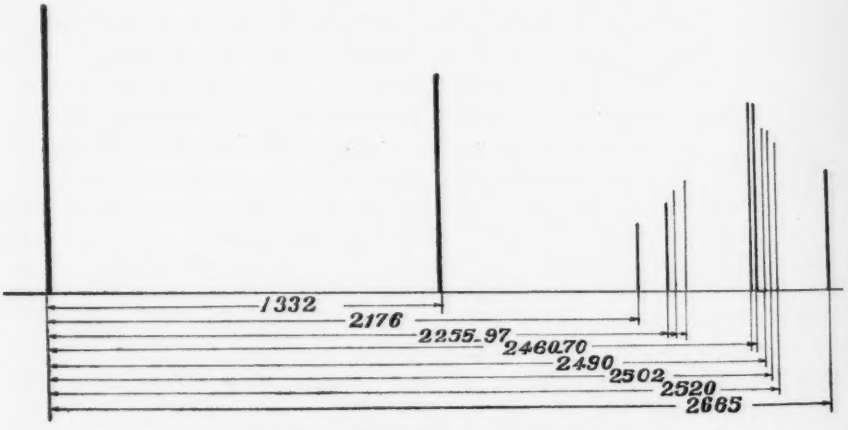



FIG. 5. Frequency shifts in light scattering.

Very conspicuous is the sharply defined peak of intensity terminating the second-order spectrum and exhibiting a frequency shift of 2665 cm.$^{-1}$ This is clearly to be identified as the octave of the principal mode of vibration having a frequency shift of 1332 cm.$^{-1}$: its measured spectral width of

8 wave numbers is also approximately double the spectral width of that frequency shift at room temperature.

Very conspicuous also in the microphotometer records is the sharply defined peak of intensity with a frequency shift of 2176 cm.$^{-1}$ This is clearly the octave of the common frequency 1088 cm.$^{-1}$ of modes V and VI listed in Table I.

Of much greater intensity than either of the peaks mentioned above is that which can be recognised both in the spectra and in the microphotometer records as a clearly resolved pair of lines whose frequency shifts are 2460 and 2470 cm.$^{-1}$ respectively. The calculated frequency of the octave of mode III in Table I is 2478 cm.$^{-1}$ and this is sufficiently close to the position of the doublet to justify our identifying the latter with it.

Close to the doublet but clearly separated from it appear a group of rather diffuse lines whose frequency shifts are 2490, 2502 and 2520 respectively. The mean of these three shifts is 2504 and we may therefore identify the triplet of lines as being the octave of mode III in Table I whose calculated value is 2500 cm.$^{-1}$

Finally, we have a group of rather inconspicuous maxima, of which the most evident is one with frequency shift of 2255 cm.$^{-1}$ followed by a series of others with larger frequency shifts. The octave of mode IV the frequency of which is 2298 cm.$^{-1}$ lies within this range.

## 7. Some Concluding Remarks

Spectroscopic investigation of the scattering of light in diamond thus decisively confirms the theoretical result that its structure possesses a discrete set of normal modes of vibration with well-defined frequencies forming a sequence as indicated in Table I. Various details revealed by the study, *viz.*, the great differences in the relative intensities with which the various modes appear and the spectral splitting which some of them exhibit are also readily explicable.

The non-appearance of modes VIII and IX as frequency shifts even in the second-order scattering is not surprising. In these modes of vibration, neighbouring atoms of carbon do not approach or recede from each other but move laterally. Hence, no very sensible variations in the optical polarisability of the structural units are to be expected. *Per contra*, the approach and recession of neighbouring carbon atoms is very conspicuous in modes I, II and III and the appearance of the octaves of these modes with notable intensities is therefore in accord with expectation. That modes II and III

appear even more strongly than mode I is clearly a consequence of their degeneracies being 8 and 6 respectively as compared with the degeneracy 3 of mode I. The strength with which the peak at 2176 cm.$^{-1}$ is recorded is likewise explicable as due to the superposition of the effect of six modes having a common frequency.

That a second-order spectrum of light-scattering is at all observable becomes intelligible when it is recalled that the oscillators which are set in vibration and diffuse the incident radiation with a diminished frequency are the structural elements in the crystal. These are of extremely small dimensions and contain relatively few atoms. Hence, the absorption by them of a quantum of energy would result in vibrations of which the amplitude cannot be considered as infinitesimally small in relation to the interatomic distances. It follows that the periodic variation of optical properties resulting from the vibration would exhibit anharmonicity. Frequency shifts corresponding to overtones and combinations of the frequencies of the normal modes can therefore appear in the scattered light. The mechanical anharmonicity associated with vibrations of finite amplitude may likewise result in the splitting up of energy levels which in the harmonic oscillator approximation can be considered as identical.

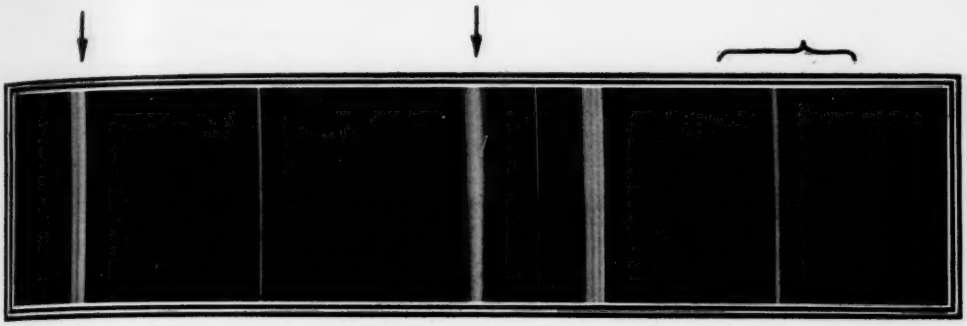


FIG. 1

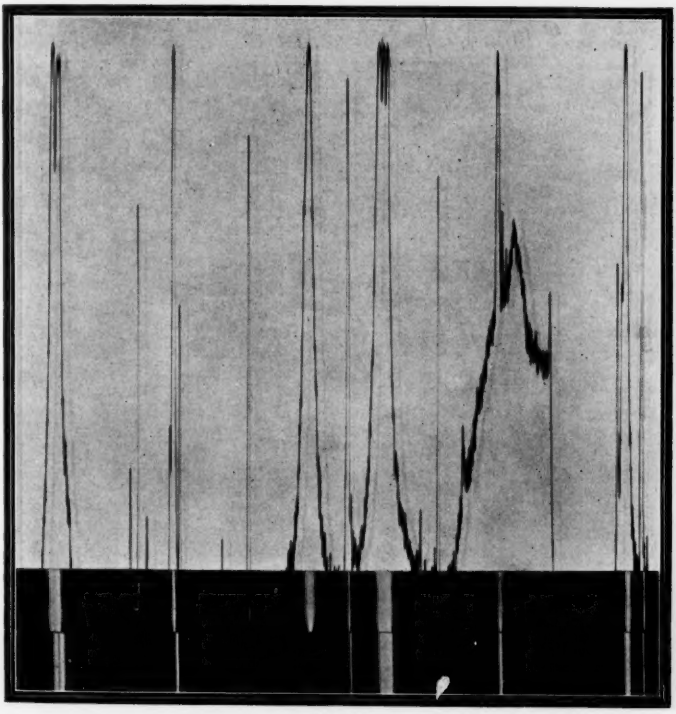


FIG. 2

Scattering of light in diamond: medium spectrograph.

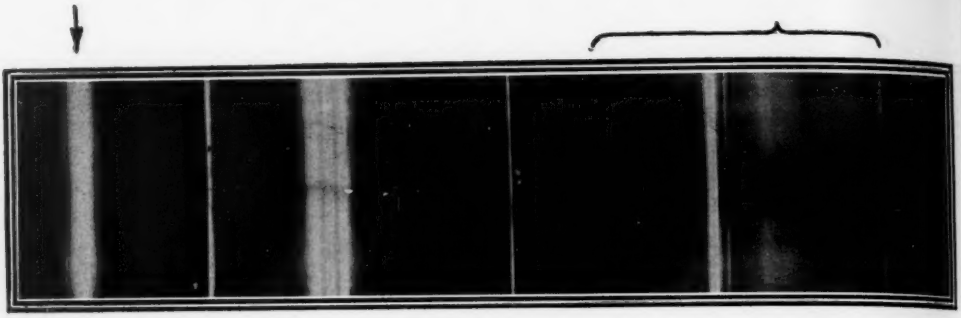


FIG. 1

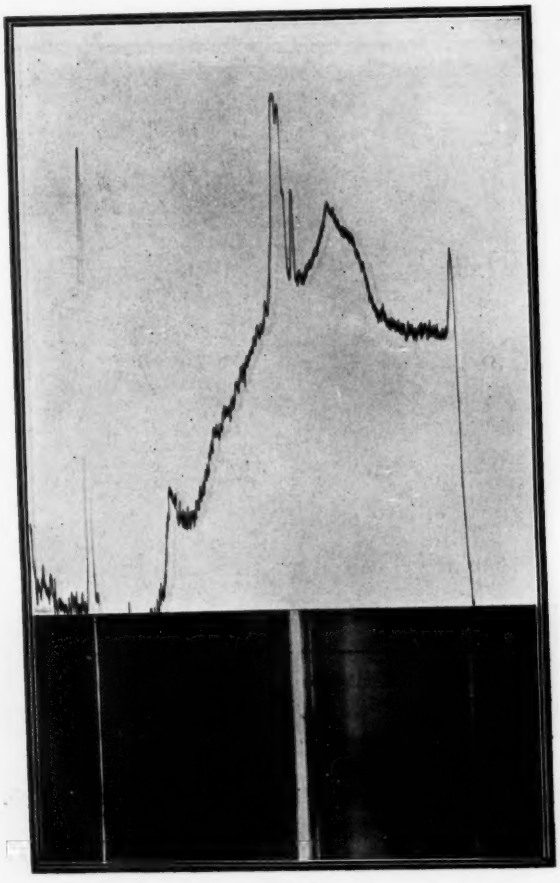


FIG. 2

Scattering of light in diamond: large spectrograph.

# DESIGN AND PERFORMANCE OF A THIN MAGNETIC LENS β-RAY SPECTROMETER

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Received July 9, 1956

(Communicated by Prof. B. Peters, F.A.SC.)

## Abstract

Construction of a thin magnetic lens β-ray spectrometer is described. A baffle system which takes advantage of the ring focus has been designed on the basis of the calculations of electron trajectories limited to an angle of acceptance of 9–10·5 degrees. The results of the study of the β-ray spectra of $Sr^{90}$ and $Y^{90}$, $Pm^{147}$, $Tm^{170}$ are presented.

## Introduction

After the early work of Klemperer[1] in constructing a thin magnetic lens β-ray spectrometer, Deutsch *et al.*[2] made considerable progress with this type of instrument and they were followed by other workers. The early designers met with the difficulty of spherical aberration when trying to use large exit angles. The idea that the use of an annular exit slit would reduce the aberration to a great extent was suggested by Frenkel.[3] This type of ring baffle was used by Zünti[4] in a lens spectrometer obtaining a resolution of 1·3% with a gathering power of 2·7%. Later, Hornyak[5] *et al.* and Verster[6] built thin lens spectrometers using the ring-focus principle. The relative simplicity of design and low cost make the thin lens spectrometer a very important feature in a nuclear spectroscopy laboratory. One such instrument has been designed and constructed in the laboratories of the Tata Institute of Fundamental Research in Bombay and is in regular operation since sometime now. This paper gives an account of its special features of design and performance.

## Technical Description

This β-ray spectrometer has been developed as part of a project to study the focusing properties of various types of magnetic lenses as applied in β-ray spectroscopy and hence, this preliminary design has been made in such a way that this spectrometer can be converted to some other type without any major constructional alterations.

* Now on leave of absence at Department of Physics, University of Wisconsin, Madison, Wisconsin.

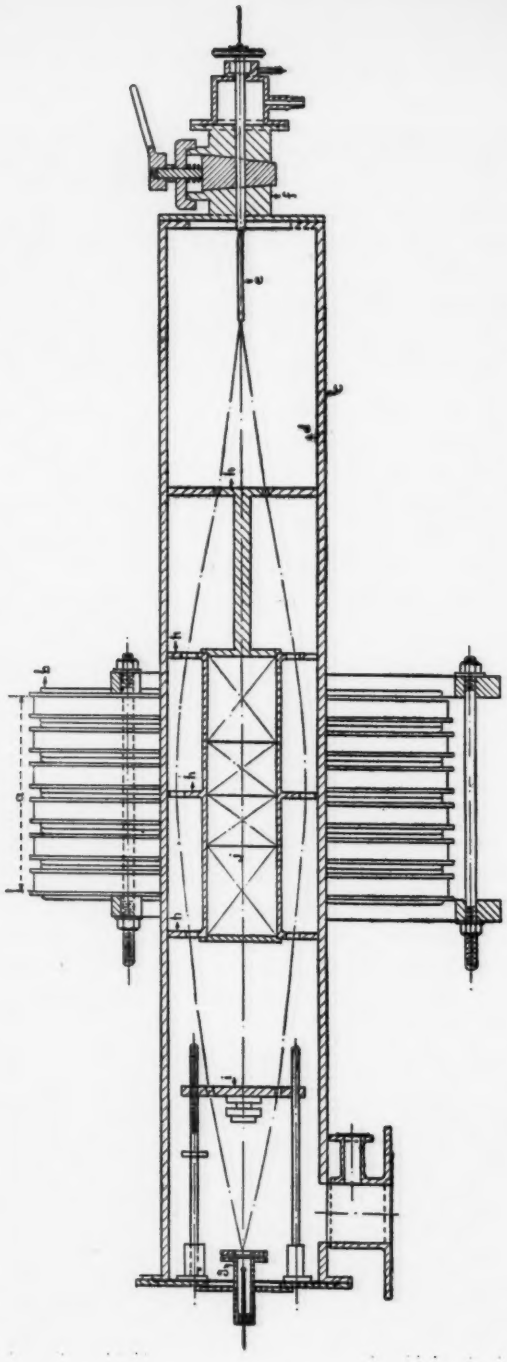


FIG. 1.

(*a*) *The Magnet* (Fig. 1 *a*).—The magnet consists of six coils of " pan-cake " design clamped together. Each coil has 66 turns of $1 \times 1/16''$ copper strip. The strips are covered with empire cloth for insulation. At present, all the six coils are connected in series. The two outer faces of each pan-cake are made out of 1/16″ brass plates and copper tubes are welded on these plates in a zig-zag fashion (*b*). A flow of water of 120 gallons per hour at room temperature (which is normally 32° C.) is maintained through these tubes. A current of 120 amps. can be passed through the coils without undue heating. This current is necessary to focus 5 MeV electrons. The total length of the lens is 29 cm. and the inner and the outer radii of the pan-cakes are 13 cm. and 34 cm. respectively. The current for the magnet is provided by a 5 KW d.c. motor-generator set. The current is stabilised by balancing the potential drop across a low resistance and the error signal is fed through a d.c. amplifier to the d.c. coils of a saturable core reactor which in its turn controls the excitation field of the generator. The performance of this stabiliser has been found to be satisfactory and the current is maintained stable to better than 1 in 1,000 over the entire energy range of the spectrometer.

A step by step numerical calcuation of the magnetic field along the axis of the lens has been made following the method of Keller *et al.* By using a snatch coil along with a flux meter, the magnetic field along the axis has also been measured. The fit of the experimental with the theoretical curve is excellent.

(*b*) *The Vacuum Tank* (Fig. 1 *c*).—The spectrometer chamber is made out of a five foot long brass tube $8\frac{3}{4}''$ i.d. and $9\frac{1}{2}''$ o.d. The inside of the tank is completely lined with 1/16″ thick aluminium sheet to minimise scattering (*d*). A vacuum of about $10^{-5}$ mm. of Hg is maintained inside the tank by a three stage Edwards Model 403 oil diffusion pump backed by a single stage rotary pump. The source holder is carried at the end of a long brass rod (*e*) which can be introduced into the chamber through a vacuum lock at one end (Fig. 1 *f*). Care is taken to avoid the presence of any iron near the spectrometer. The alignment between the chamber axis and the magnetic axis has been made by carefully introducing shims between the body of the tank and the body of the magnet, the clearance being extremely small between the two. An end window type of G–M counter is used as the detector for the electrons (*g*). The filling system is so arranged that the counter can be filled up *in situ* without letting the pressure difference between the inside and the outside of the counter become more than a few cm. The gas mixture used in the counter is 40 mm. Argon and 12 mm.

alcohol. Windows generally used are 1 mg./cm.$^2$ mica or formvar. The G–M counter is being currently replaced by a scintillation counter.

To avoid the scattered electrons from entering the detector as well as to properly define the trajectories of the focused electrons inside the tank, a system of baffles is used (*h*). For designing this baffle system, a step by step numerical calculation of the trajectories of the electrons in the magnetic field used was made following Keller *et al.*[7] This calculation also indicated the position of the ring focus. The entire baffle system is made of 3/16″ thick aluminium excepting the annular ring baffle which is made of ½″ thick Perspex (*i*). At the centre of the chamber a five-inch long lead block (*j*) is placed to shield the counter from direct radiations. To start with, the ring baffle was carried by two bars sticking out inside the chamber along which it could be moved. Once the correct position was experimentally determined, the baffle was firmly fixed there. The width of the exit slit is designed to be equal to the diameter of the source used which can be either 6 mm. or 3 mm.

## PERFORMANCE

(*a*) *Calibration.*

The spectrometer was calibrated by measuring the 637 KeV $\gamma$-line of $Ba^{137}$. The sample used was of 6 mm. diameter and was mounted on ·5 mg./cm.$^2$ mica. The resolving power of the instrument from this measurement was found to be

$$\eta = \frac{\Delta H\rho}{H\rho} = 2{\cdot}8\%.$$

The gathering power of the spectrometer as calculated from the geometry of the instrument

$$\omega = \frac{\Omega}{4\pi} = 0{\cdot}54\%.$$

The luminosity of the spectrometer

$$L = \sigma\omega \text{ (where } \sigma \text{ is the area of the source)}$$
$$= 6{\cdot}2\times10^{-3} \text{ cm.}^2$$

Perisco and Geoffrion[8] defined two dimensionless quantities $\Phi$ and $\Psi$ as figures of merit of helical $\beta$-ray spectrometers where

$$\Phi = \eta^{-5/2}\frac{L}{l^2}.$$

$l$ being the distance between the source and the detector.

$$\Psi = \eta^{-1}\omega$$

For our spectrometer

$$\Phi = 3{\cdot}5\times10^{-3} \text{ and } \Psi = 3{\cdot}4\times10^{-2}.$$

These figures compare very favourably with those of other spectrometers of this type (*vide* Perisco and Geoffrion,[8] Table III). Use of a source of 3 mm. diameter along with an annular exit slit of 3 mm. width would bring down the value of $\eta$ to $< 2\%$.

(*b*) *Measurement of β-spectra*

(i) $Sr^{90}-Y^{90}$.—These two activities with half-lives of 19·9 *y* and 64·2 *h* are in equilibrium with each other. The $\beta^-$-spectra have been investigated by a few workers,[9, 10] all of whom seem to agree that both the spectra are of the unique first forbidden shape ($\Delta I = 2$, yes). Glendenin *et al.*[11] reported to have found no gamma in the decay of $Sr^{90}$. Saraf *et al.*[12] and Johnson *et al.*[13] observed no photons in the decay of $Y^{90}$. However, Johnson *et al.*[13] reported to have observed conversion electrons of 1·75 MeV indicating a 0—0 transition.

The source used in our measurement was a neutron irradiated composite source of $Sr^{89, 90}$ obtained from Harwell. Our measurements were started after the activity due to $Sr^{89}$ had died down to negligible intensity. The sample for the spectrometer was made by evaporating a drop of the solution on a thin backing of mica. The measured β-spectrum and the corresponding Fermi-Kurie plot corrected by the Gamow-factor

$$G = \sum_{\nu=0}^{n} \frac{(2n+1)!\,(2\nu+1)!}{2^{2\nu}\,(\nu!)^2\,(2n-2\nu+1)!}\, q^{2(n-\nu)}\, L_\nu$$

is reproduced in Figs. 2, 3 and 4. We have found for $Sr^{90}$

$$E_{\beta\ max.} = 0{\cdot}541 \pm 0{\cdot}008 \text{ MeV}$$

and for $Y^{90}$

$$E_{\beta\ max.} = 2{\cdot}28 \pm 0{\cdot}03 \text{ MeV}$$

and the transition probabilities are

$\log (W_0^2 - 1)\, ft = 9{\cdot}7$ and $\log (W_0^2 - 1)\, ft = 9{\cdot}5$ respectively.

These values are in agreement with the measurements of other workers. Investigations on the 1·75 MeV 0—0 transition are in progress.

(ii) $Pm_{86}^{147}$.—Langer *et al.*[14] and Agnew[15] have studied the β-spectrum due to this isotope and Boehm and Wu[16] have studied the inner brehmstrahlung. Several workers have reported to have found no γ-radiations.

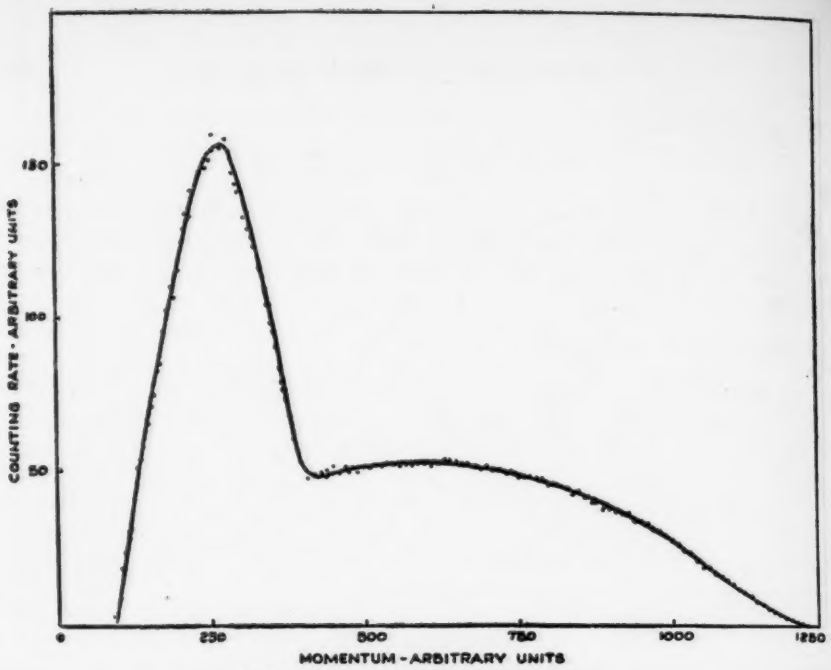


FIG. 2. $Sr^{90}$ and $Y^{90}$ Total $\beta$-Spectrum.

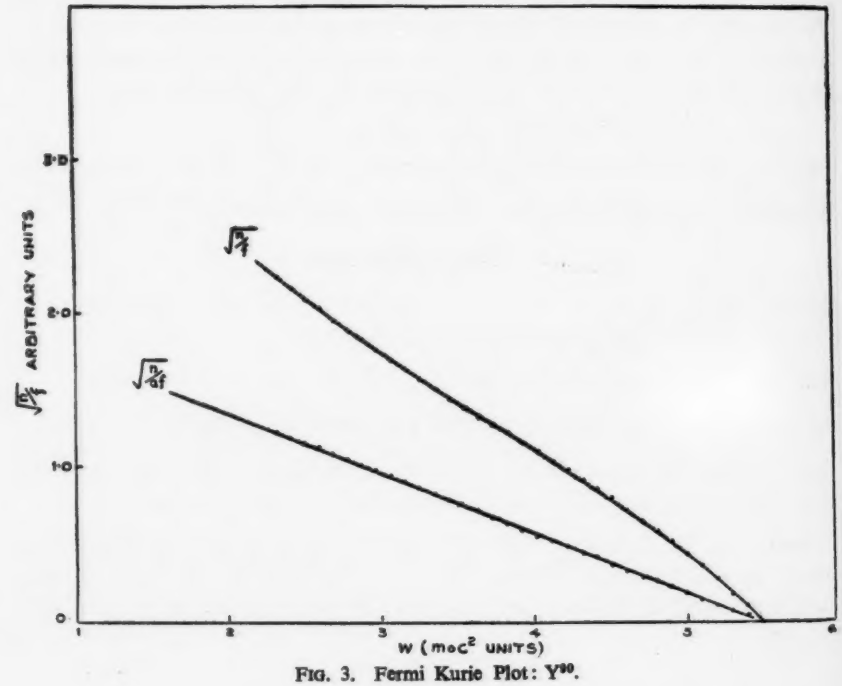


FIG. 3. Fermi Kurie Plot: $Y^{90}$.

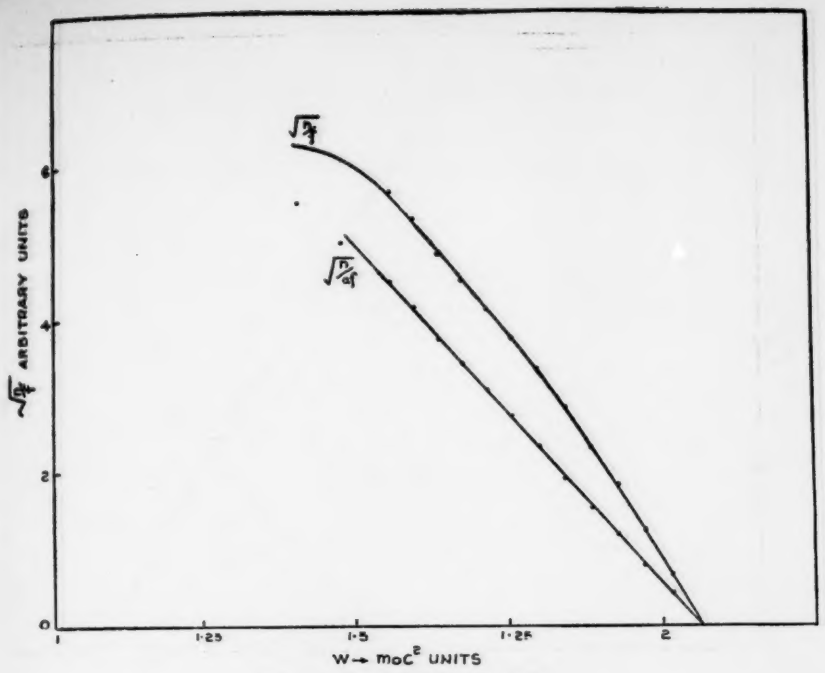


FIG. 4. Fermi Kurie Plot: $Sr^{90}$.

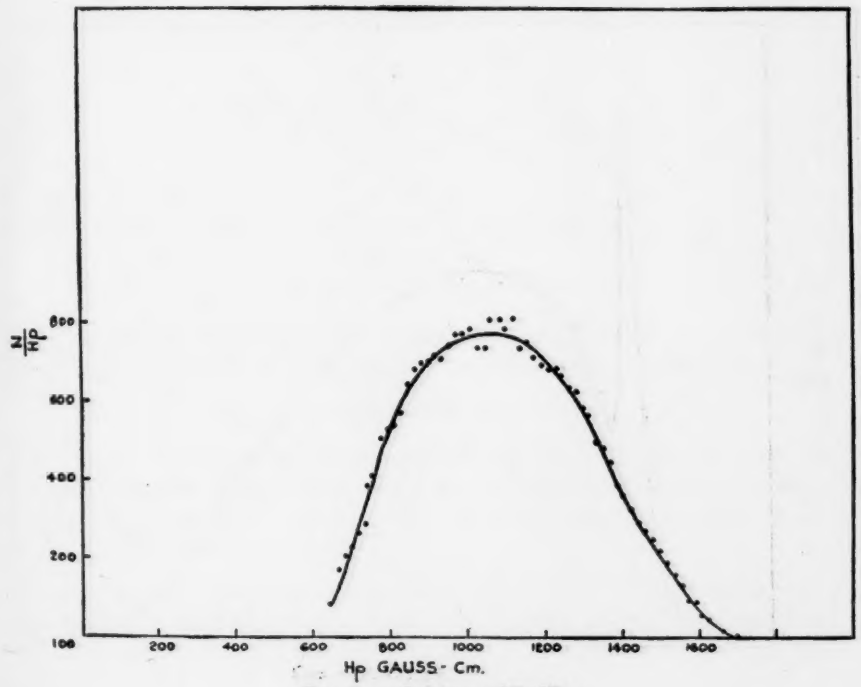


FIG. 5. β-Spectrum of $Pm^{147}$.

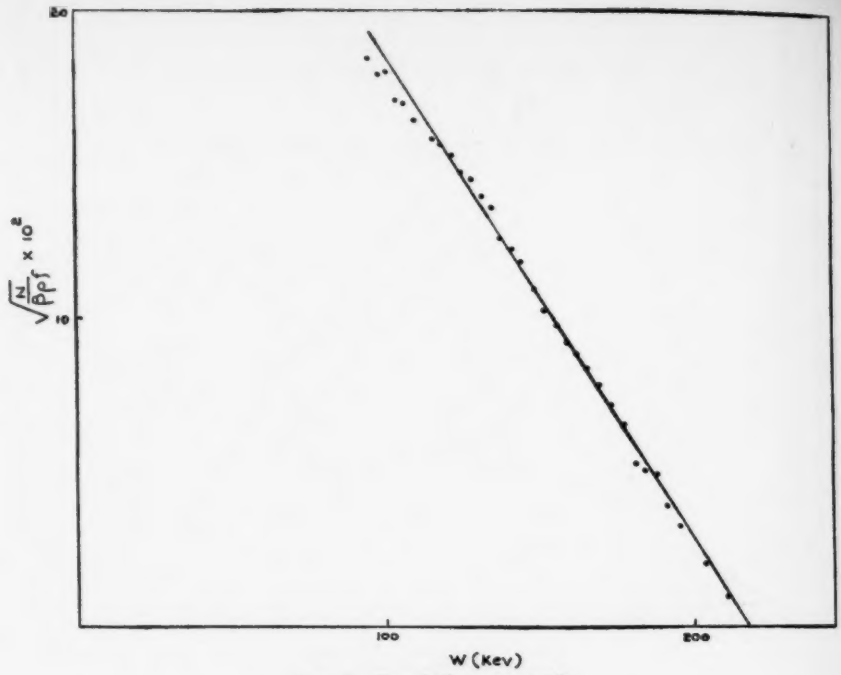


FIG. 6. Fermi Plot of $_{61}Pm^{147}$.

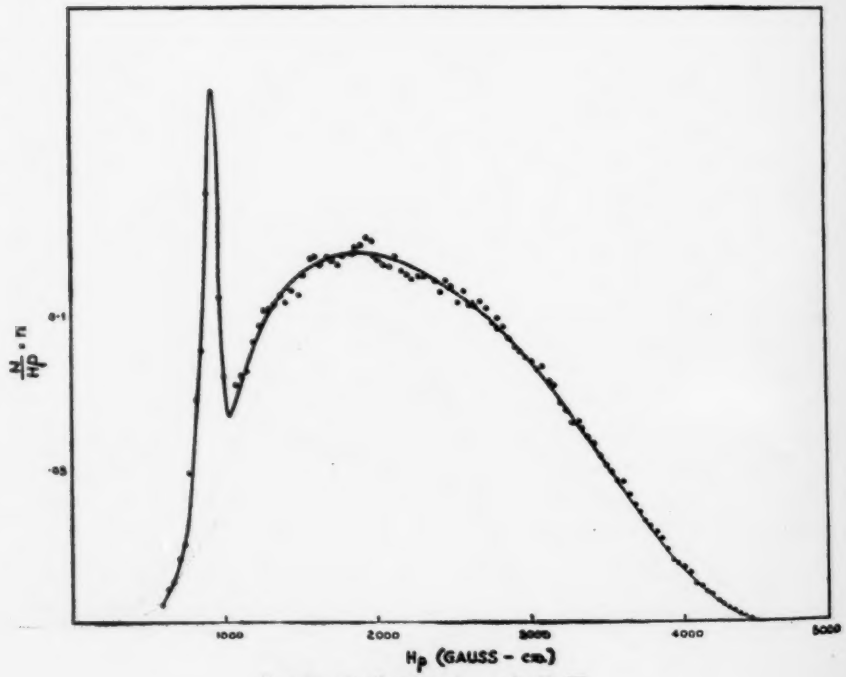


FIG. 7. Total $\beta$-Spectrum of $_{69}Tm^{170}$.

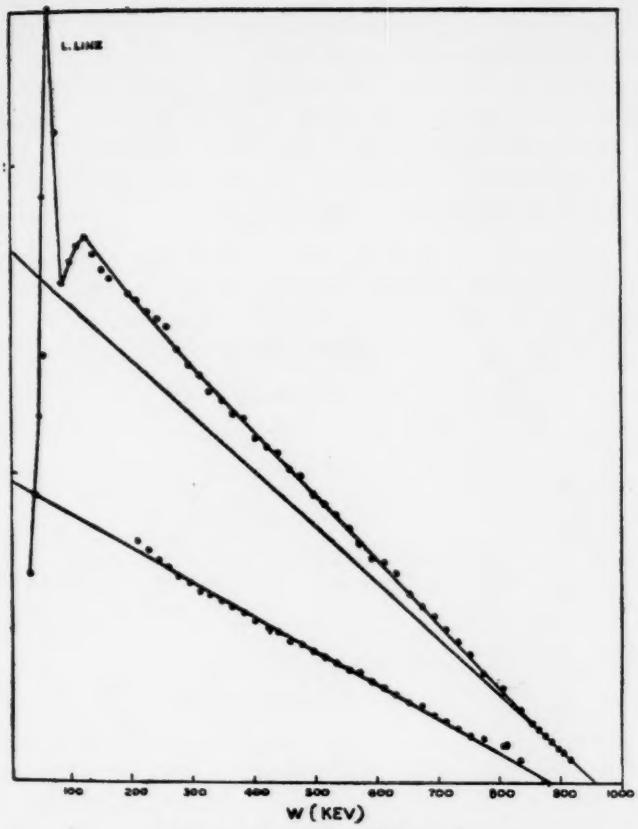


FIG. 8. Fermi Kurie Plot of $Tm^{170}$.

We have studied the $\beta^-$-spectrum in our spectrometer (Fig. 5). From the Fermi-Kurie plot (Fig. 6) one sees that the spectrum is simple and

$$E_{\beta\ max.} = 0{\cdot}218 \pm 0{\cdot}005\ \text{MeV}$$

The "$\log ft$" is calculated to be equal to $\log ft = 7{\cdot}5$. The $\beta$-transition is from the ground state of $Pm^{147}$ to the ground state of $Sm^{147}$ and therefore, is from a $d_{5/2}$ state to a $f_{7/2}$, *i.e.*, $\Delta I = 1$, yes. The $\log ft$ value is in agreement with this class of transition.

(iii) $Tm_{101}^{170}$.—This isotope has been carefully studied by Graham *et al.*[17] and they have established a decay-scheme which is slightly different from

that given by Fraser.[18] Several other workers have also studied this nuclide and the reader is referred to the former paper for complete reference. Our sample was irradiated in the reactor of AERE, Harwell. The source was prepared on a backing of mica. The measured $\beta$-spectrum and the Fermi-Kurie plot are reproduced in Figs. 7 and 8. From the Kurie plot, it can be seen that the $\beta$-spectrum is complex and can be resolved into two partial spectra of $E_{\beta\,max.} = 0{\cdot}957 \pm 0{\cdot}007$ and $E_{\beta\,max.} = {\cdot}882 \pm 0{\cdot}010$. The relative

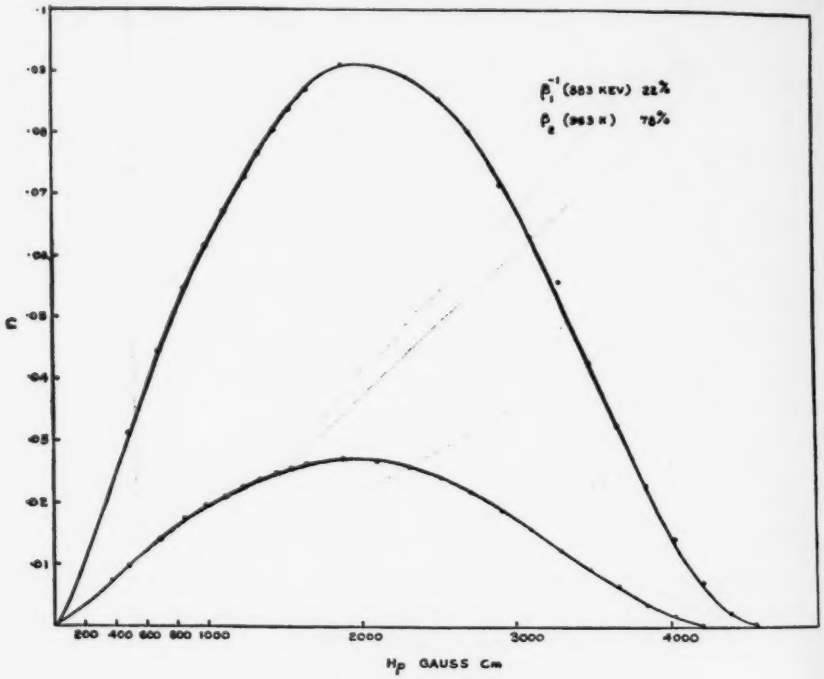


FIG. 9. $Tm^{170}$ Relative Intensities of $\beta$-Groups.

intensities of these two partial spectra are 78% and 22% respectively (Fig. 9). This confirms the decay-scheme of Graham *et al.*[17] Fraser[18] had reported the relative intensities to be 90% and 10%. Superimposed on the $\beta$-spectrum is the L-conversion line (unresolved $L_I$, $L_{II}$, $L_{III}$ and M) due to an 84 KeV $\gamma$-transition. Graham *et al.* have established the nature of this transition to be E2. The log *ft* values of the two partial spectra are 9·3 and 8·9 which place them in the category of first forbidden transitions. Therefore spin assignments of $2^+$ to the 84 KeV level of $Yb^{170}$ and $1^-$ to the ground state $Tm^{170}$ can be made, the ground state spin of $Yb^{170}$ being $0^+$.

## Discussion

In this preliminary design of the spectrometer good resolving power along with moderate gathering power for this class of instruments have been achieved. In a future alteration, it will be aimed at to use a larger incident angle ($> 20°$) without losing much of the resolving power. It is also proposed to split the single lens into two lenses and to shorten the distance between the source and the counter. Some studies will also be made of the use of auxiliary baffles to the single ring baffle as done by P. Hubert[19] and de Waard.[20]

The authors wish to take this opportunity of thanking Dr. H. J. Bhabha, F.R.S., the Director of the Tata Institute, for the stimulating interest he has taken in this work. The kind co-operation of the members of the workshop is also gratefully acknowledged.

## References

1. Klemperer, G. .. *Phil. Mag.*, 1935, **20**, 545.
2. Deutsch, M., Elliot, L. G. and Evans, R. D. *Rev. Sc. Inst.*, 1944, **15**, 178.
3. Frenkel, S. .. *Phys. Rev.*, 1948, **73**, 804.
4. Zünti, W. .. *Helv. Phys. Acta*, 1948, **21**, 179 A.
5. Hornyak, W. F., Lauritssen, T. and Rasmussen, V. K. *Phys. Rev.*, 1949, **76**, 731.
6. Verster, N. F. .. *Appl. Sc. Research*, 1950, **1 B**, 363; *Physica*, 1951, **17**, 637.
7. Keller, J. M., Konigsberg, E. and Paskin, A. *Rev. Sc. Instr.* 1950, **21**, 713.
8. Perisco, E. and Geoggrion, C. *Ibid.*, 1950, **21**, 945.
9. Laslett, L. J., Jensen, E. N. and Paskin, A. *Phys. Rev.*, 1950, **79**, 412.
10. Moreau, J. and Peresy Jorba, J. *Compt. rend.*, 1952, **235**, 38.
11. Glendenin, L. E. and Coryell, C. E. *NNES*, 1950, **9**, 667.
12. Saraf, B., Varma, J. and Mandeville, C. E. *Phys. Rev.*, 1955, **98**, 1206 A.
13. Johnson, O. E., Johnson, R. G. and Langer, L. M. *Ibid.*, 1955, **98**, 1517.

14. Langer, L. M., Motz, J. W. and Price, H. C. *Phys. Rev.*, 1950, **77**, 798.

15. Agnew, H. M. .. *Ibid.*, 1950, **77**, 655.

16. Boehm, F. and Wu, C. S. *Ibid.*, 1954, **93** (3), 518.

17. Graham, R. L., Wolfson, J. E. and Bell, R. E. *Can. J. Phys.*, 1952, **30**, 459.

18. Fraser, J. S. .. *Phys. Rev.*, 1949, **76**, 1540.

19. Hubert, P. .. *Physica*, 1952, **18**, 1129.

20. de Waard, H. .. Thesis, Groningen, 1954.

# HETEROCYCLIC COMPOUNDS

## Part VII.* Synthesis of 2-Quinolyl Benzimidazoles

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Received July 6, 1956

(Communicated by Dr. K. N. Menon, F.A.SC.)

A large number of carboxylic acids have been condensed with *o*-phenylene diamine to give derivatives of benzimidazoles.[1, 2, 3] This report relates to the synthesis of all the seven 2-quinolyl benzimidazoles obtained by condensing the quinoline-carboxylic acids with equimolecular quantities of *o*-phenylenediamine. In the case of quinoline-3-carboxylic acid, considerable decarboxylation took place during the condensation reaction and the benzimidazole was obtained only in poor yields. Quinoline was recovered.

It is interesting to note that Miklaszewski and Niementowski[4] reported the synthesis of 2-(quinolyl-6), 2-(quinolyl-5 or 7) and 2-(quinolyl-8) benzimidazoles, starting from the properly substituted 2-aminophenyl-benzimidazoles and building up the quinoline nucleus by Skraup reaction. The method adopted in the work under report has the advantage of simplicity. Some discrepancy is found between the reported melting point of 2-(quinolyl-8)-benzimidazole and what is reported in the present work. Again, what has been reported as 2-(quinolyl-5 or 7)-benzimidazole corresponds neither to 2-(quinolyl-5) nor to 2-(quinolyl-7) benzimidazole now obtained. This discrepancy requires further examination and is engaging attention.

### Experimental

*2-(Quinolyl-2)-benzimidazole*

Quinaldinic acid (3 g.) was mixed with *o*-phenylenediamine (2 g.) and the mixture maintained at 180° to 190° C. for one hour in an oil-bath. The product was cooled, dissolved in dilute hydrochloric acid (1 : 1), filtered and basified with ammonia under cooling, to give the benzimidazole (3 g.). Dark grey needles of m.p. 213° C. from ethanol.

Found: N, 17·23%. $C_{16}H_{11}N_3$ requires N, 17·14%.

The picrate of this base separated from glacial acetic acid in greenish yellow crystals of m.p. 276° C.

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* Part VI: *Proceedings*, Vol. XLII, No. 6, Sec. A, 1955, p. 289.

Found: N, 18·18%. $C_{16}H_{11}N_3 \cdot 2\,C_6H_3O_7N_3$ requires N, 17·93%.

2-(*Quinolyl*-3)-*benzimidazole*

A mixture of quinoline-3-carboxylic acid (2 g.) and *o*-phenylenediamine (1·4 g.) was maintained at 210° to 220° C. for an hour and then worked as in the previous case. The pasty product was triturated with chloroform when most of it went into solution leaving about 50 mgm. of a violet powdery substance which was collected and dried. Its crystallisation proved difficult, but the picrate crystallised from glacial acetic acid in dark green plates of m.p. 255° C.

Found: N, 17·87%. Theory: N, 17·93%.

2-(*Quinol*-4-*yl*-)-*benzimidazole*

Cinchoninic acid (1·5 g.) and *o*-phenylenediamine (1 g.), held at 190° to 200° C. for an hour, gave 1·6 g. of the benzimidazole, dark grey needles from dilute methanol, m.p. 216° C.

Found: N, 17·29%. Theory: N, 17·14%.

Picrate, m.p. 236° C. from acetic acid.

Found: N, 17·75%. Theory: N, 17·93%.

2-(*Quinol*-5-*yl*)-*benzimidazole*

Quinoline-5-carboxylic acid (1·5 g.) and *o*-phenylenediamine (1 g.) held at 250° to 260° C. for one and a half hours gave 1 g. of the benzimidazole. The crude product was extracted with hot ethyl acetate and crystallised from toluene. Yellow crystalline powder m.p. 255° C.

Found: N, 16·76%. Theory: N, 17·14%.

The picrate crystallised from glacial acetic acid in bright yellow plates of m.p. 228° C.

Found: N, 17·52%. Theory: N, 17·93%.

2-(*Quinol*-6-*yl*)-*benzimidazole*

Quinoline-6-carboxylic acid (4 g.) and *o*-phenylenediamine (2·5 g.) held at 220° C. for an hour, gave 2 g. of the benzimidazole. Yellow crystalline powder of m.p. 221° C. from toluene.

Found: N, 17·12%. Theory: N, 17·14%.

The picrate was obtained in bright yellow crystals of m.p. 262° C. from glacial acetic acid.

Found: N, 17·99%. Theory: N, 17·93%.

*2-(Quinol-7-yl)-benzimidazole*

Quinoline-7-carboxylic acid (3 g.) and *o*-phenylenediamine (2 g.) maintained at 200° to 210° C. for an hour gave 3 g. of the benzimidazole. Light violet needles from dilute methanol, m.p. 273° C.

Found: N, 16·9%. Theory: N, 17·14%.

The picrate was obtained as bright yellow crystals from acetic acid, m.p. 293° C.

Found: N, 18·25%. Theory: N, 17·93%.

*2-(Quinol-8-yl)-benzimidazole*

Quinoline-8-carboxylic acid (2·6 g.) and *o*-phenylenediamine (1·6 g.) held at 210° to 220° C. for one and a half hours gave 1·5 g. of the benzimidazole. Reddish brown needles from dilute methanol, m.p. 118° C. The crystalline base turned amorphous brown on vacuum drying at 80° C. and melted at 108° C. The dried product analysed for N, 16·81% as against theory 17·14%.

The picrate melted at 273° C. after crystallisation from acetic acid.

Found: N, 17·94%. Theory: N, 17·93%.

## Summary

The synthesis of seven isomeric 2-quinolyl-benzimidazoles is reported.

## Acknowledgement

I am deeply indebted to Dr. K. N. Menon for guidance. I am thankful to Dr. T. R. Govindachari for permission to carry out the analysis in his laboratory and to Mr. S. Selvavinayakam for help in the analysis and to the Government of India for the award of a Junior Research Scholarship.

## References

1. Wright, J. B. .. *Chemical Reviews*, 1951, **48**, 402.
2. Bastic, B. L. .. *Chem. Abstracts*, 1954, **48**, 5860 *e*.
3. Porai-Koshits, B. A., *et al.* *Ibid.*, 1948, **42**, 5903 *f*.
4. Bol. Miklaszewski and St. von Niementowski *Ber.*, 1901, **34**, 2973.

# HETEROCYCLIC COMPOUNDS

## Part VIII.* Synthesis of 1-Quinolyl Isoquinolines

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Received July 6, 1956

(Communicated by Dr. K. N. Menon, F.A.SC.)

Synthesis of isoquinolines with pyridine and quinoline groups in position-I have been reported.[1, 2] The present work records the synthesis of seven 1-quinolyl-3-methyl-3 : 4-dihydro-6 : 7-methylenedioxy-isoquinolines by standard methods.

### Experimental

*α-Methyl homopiperonylamine*

This amine was prepared by a new route. Piperonal was condensed with nitroethane and the nitrostyrene[3] reduced to the amine with lithium aluminium hydride. Powdered lithium aluminium hydride (4·5 g.) was suspended in dry ether (200 c.c.) and to the vigorously stirred suspension a solution of the nitro-styrene in dry ether (200 c.c.) was added in the course of an hour, external ice cooling being employed to control the reaction. The mixture was stirred for 10 hours, after which the excess of the metallic hydride was destroyed and the mixture poured into a well stirred mixture of ice and 10% sulphuric acid. The acidic aqueous layer was separated basified with 10% sodium hydroxide solution, under cooling, the amine taken up in isopropyl ether, dried and ether removed, yielding 4·4 g. of the pure amine of b.p. 152° C./17 mm.

*2′-Quinolyl-α-methyl-β-3 : 4-methylenedioxy phenyl ethyl amide*

To α-methyl homopiperonyl amine (4 g.) in dry benzene (40 c.c.) was added slowly with constant shaking, quinaldinic acid chloride hydrochloride (2·3 g.) and the mixture refluxed on the water-bath for 4 hours. The benzene layer was then filtered hot from an insoluble residue, evaporated to dryness and the amide (2 g.) crystallised from light petrol. Colourless plates, m.p. 116° C.

Found: N, 8·68%. Theory: N, 8·39%.

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* Part VII: *Proceedings*, Vol. XLIV, No. 3, Sec. A, 1956, p. 123.

1-(2′ *Quinolyl*)-3-*methyl*-3 : 4-*dihydro*-6 : 7-*methylenedioxy-isoquinoline*

The above amide (1 g.) in dry benzene (30 c.c.) was treated with posphorous oxychloride (3 c.c.) and the mixture refluxed on the water-bath for 4 hours. The cooled solution was poured into ice water, aqueous layer separated and basified with ammonia to yield the isoquinoline (0·6 g.). Colourless plates, m.p. 141° C. from light petrol.

Found: N, 8·87%. Theory: N, 8·86%.

3′-*Quinolyl-α-methyl-β*-3 : 4-*methylenedioxy phenyl ethyl amide*

The homopiperonylamine (3 g.) in dry benzene (30 c.c.) was treated gradually with quinoline-3-carboxylic acid chloride hydrochloride (1·8 g.) and the mixture refluxed for 4 hours. The benzene solution was evaporated and the residue extracted with dilute hydrochloric acid. Basification of the filtered aqueous extract with ammonia precipitated the amide as a paste which solidified on standing. Crystallisation from dilute ethanol gave clustrous needles (1·3 g.) of m.p. 110°–114° C., which on drying in vacuum over phosphorous pentoxide for two days melted sharply at 128° C.

Found: N, 8·61%. Theory: N, 8·39%.

The picrate of this amide melted at 182° C. (from acetic acid).

Found: N, 12·15%. Theory: $C_{20}H_{18}O_3N_2 \cdot C_6H_3O_7N_3$—N, 12·44%.

1-(3′-*Quinolyl*-)-3-*methyl*-3 : 4-*dihydro*-6 : 7-*methylenedioxy isoquinoline*

Cyclisation of the amide (1 g.) was effected in gently refluxing toluene, with phosphorous oxychloride (5 c.c.). The toluene was removed, the residue taken up in water, filtered and basified with ammonia. The isoquinoline (0·5 g.) crystallised in colourless clusters from dilute methanol, m.p. 98°–100° C.

Found: N, 9·14%. Theory: N, 8·86%.

The picrate, golden yellow needles from methanol, melted at 201° C.

Found: N, 14·56%. Theory: N, 14·47%.

4′-*Quinolyl-α-methyl-β*-3 : 4-*methylenedioxy phenyl ethyl amide*

This amide was obtained by condensing the homopiperonyl amine with cinchoninic acid chloride hydrochloride in dry benzene or by maintaining equal quantities of the amine and cinchoninic acid ethyl ester at 140° C. for 20 hours. The amide crystallised in white leaflets from acetone, m.p. 144° C.

Found: N, 8·58%. Theory: N, 8·39%.

The picrate yellow needles from ethanol, m.p. 204° C.

Found: N, 12·6%. Theory: N, 12·44%.

1-(4′-*Quinolyl*)-3-*methyl*-3 : 4-*dihydro*-6 : 7-*methylenedioxy isoquinoline*

The base obtained on cyclization of the amide could not be crystallised, but the picrate crystallised from methanol as yellow plates of m.p. 202° C. A mixture of this picrate and the picrate of the amide (m.p. 204° C.) melted at 186° C.

Found: N, 14·34%. Theory: $C_{20}H_{16}O_2N_2 \cdot 2C_6H_3O_7N_3$: N, 14·47%.

5′-*Quinolyl*-α-*methyl*-β-3 : 4-*methylenedioxy phenyl ethyl amide*

The homopiperonyl amine (4 g.) and quinoline-5-carboxylic acid chloride hydrochloride (1·8 g.) gave the amide (1·5 g.). White needles from benzene-light petrol, m.p. 173° C.

Found: N, 8·45%. Theory: N, 8·39%.

1-(5′-*Quinolyl*)-3-*methyl*-3 : 4-*dihydro*-6 : 7-*methylenedioxy isoquinoline*

The base obtained by cyclization of the amide remained pasty. The picrate separated from ethanol in yellowish green prisms, m.p. 175° C. (decomp.).

Found: N, 14·43%. Theory: N, 14·47%.

6′-*Quinolyl*-α-*methyl*-β-3 : 4-*methylenedioxy phenyl ethyl amide*

The homopiperonyl amine and quinoline-6-carboxylic acid chloride hydrochloride afforded the amide, colourless plates from light petrol, m.p. 142° C.

Found: N, 8·67%. Theory: N, 8·39%.

1-(6′-*Quinolyl*)-3-*methyl*-3 : 4-*dihydro*-6 : 7-*methylenedioxy isoquinoline*

1·2 g. of the above amide gave 0·8 g. of the isoquinoline, colourless prisms from light petrol, m.p. 122° C.

Found: N, 9·14%. Theory: N, 8·9%.

7′-*Quinolyl*-α-*methyl*-β-3 : 4-*methylenedioxy phenyl ethyl amide*

This amide was prepared by employing the ester as well as the acid chloride of quinoline-7-carboxylic acid. White leaflets from acetone, m.p. 165° C.

Found: N, 8·56%. Theory: N, 8·39%.

1-(7′-*Quinolyl*-)-3-*methyl*-3 : 4-*dihydro*-6 : 7-*methylenedioxy isoquinoline*

The base from the ring closure of the amide, crystallised from light petrol in white prisms, m.p. 140° C.

Found: N, 9·17%. Theory: N, 8·86%.

8′-*Quinolyl*-α-*methyl*-β-3 : 4-*methylenedioxy phenyl ethyl amide*

This amide was obtained as a liquid and it was characterised as the picrate, yellow plates, m.p. 177° C. (from toluene).

Found: N, 12·55%. Theory: N, 12·44%.

1-(8′-*Quinolyl*)-3-*methyl*-3 : 4-*dihydro*-6 : 7-*methylenedioxy isoquinoline*

The above oily amide was subjected to ring closure without further purification. The isoquinoline was obtained as colourless plates from methanol, m.p. 164° C.

Found: N, 9·03%. Theory: N, 8·86%.

SUMMARY

The synthesis of seven 1-quinolyl-3 : 4-dihydro-3-methyl-6 : 7-methylene dioxy isoquinolines is reported and a new method of obtaining α-methyl-homopiperonyl amine described.

ACKNOWLEDGEMENT

I wish to thank Dr. T. R. Govindachari and Mr. S. Selvavinayakam for analytical facilities, the Government of India for the award of a Junior Scholarship and Dr. K. N. Menon for guidance.

REFERENCES

1. Hey, D. H. and Williams, J. M. — *J. Chem. Soc.*, 1951, 1527.
2. Alamela, B. S. and Dey, B. B. — *Proc. Natl. Inst. Sci.* (*India*), 1941, **7**, 207.
3. Knoevenagal, E. and Walter, L. — *Ber.*, 1906, **39**, 2329.

# AN X-RAY STUDY OF NATURAL MONAZITE

## II. Single Crystal Data on Indian Monazite Mineral

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Received July, 28, 1956

(Communicated by Dr. H. J. Bhabha, F.R.S., F.A.SC.)

### Introduction

In a previous communication[1] from this laboratory data obtained from a powder pattern on monazite were presented. It was shown that naturally occurring monazite containing thorium was metamict and that the order could be restored by heating at about 1100° C. for 24 hours, as evidenced by the greater sharpness of the powder pattern and the change in the density and refractive index of the heated sample. Work has now been extended to single crystal study of natural monazite and the present communication gives the cell dimensions and indices of reflecting planes obtained from the rotation and Weissenberg photographs.

The earliest X-ray study of monazite appears to have been reported in Klochmann's *Lehrbuch der Minerologie*.[2] Gliszczynski[3] studied the rotation and oscillation photographs of a single crystal of turnerite ($CePO_4$) and employed the data of Klochmann in indexing the planes. Parrish[4] used the thorium-free monazite, found by analysis to correspond to $La_4Ce_4Y(PO_4)_9$, for an independent determination of its unit cell and the space group from Weissenberg photographs. It is noteworthy that both the above single crystal studies have been made on material free from thorium.

### Experimental

Monazite is found to occur abundantly amongst the minerals in the beach sand of Travancore in South India. It is in the form of fine golden yellow grains. Several thousand particles were carefully examined under the microscope but none showed any faces or edges. A massive piece of monazite rock weighing several grams was supplied to the authors by the Raw Materials Division* of the Department of Atomic Energy, New Delhi. It looked quite homogeneous. It was a dull brown piece showing the following faces:—

* The authors are grateful to Dr. D. N. Wadia for supplying the raw material for this investigation.

$(\bar{1}\ 0\ 1)$, $(\bar{1}\ \bar{1}\ 1)$, $(\bar{1}\ 0\ 0)$, $(\bar{1}\ \bar{1}\ 0)$

$(1\ \bar{1}\ 0)$, $(1\ \bar{1}\ \bar{1})$, $(1\ 0\ 0)$, $(1\ 0\ \bar{1})$

A piece was carefully cut and used for single crystal work. A portion was used for powder pattern and some for chemical and spectroscopic analysis. The portion used for mounting was about 2 mm $\times$1 mm $\times$0·5 mm. The following photographs were taken:—

*b-axis* (i) oscillation (Fig. 1).

(ii) Weissenberg zero layer (Fig. 3).

(iii) Weissenberg 1st layer (Fig. 4) and 2nd layer by equi-inclination method.

*a-axis* (i) Rotation (Fig. 2).

(ii) Weissenberg zero layer, 1st layer equi-inclination.

From the photographs given in the figures the following cell dimensions were calculated:—

$$a_0 = 6{\cdot}66\ \text{Å}$$
$$b_0 = 6{\cdot}98\ \text{Å}$$
$$c_0 = 6{\cdot}32\ \text{Å}$$
$$\beta = 76°\ 38'$$

The density of the sample was experimentally determined with a pyknometer as 5·23 gm./c.c.

Table I gives the comparative values of the cell parameters for the thorium-bearing monazite used here and the thorium-free monazite used by previous workers.

TABLE I

| | Th-bearing | Turnerite $CePO_4$ (Gliszczynski) | Th-free monazite $La_4Ce_4Y(PO_4)_9$ Parrish |
|---|---|---|---|
| $a_0$ | 6·66 | 6·78 | 6·76 |
| $b_0$ | 6·98 | 6·99 | 7·00 |
| $c_0$ | 6·32 | 6·44 | 6·42 |
| $\beta$ | 76° 38′ | 76° 22′ | 76° 50′ |
| $\rho$ | 5·23 | 5·217 | 5·17 |

The reflecting planes indexed from the Weissenberg photographs together with the visual estimates of their intensities are collected together in Table II.

TABLE II

| *hkl* | $I/I_0$ | *hkl* | $I/I_0$ | *hkl* | $I/I_0$ | *hkl* | $I/I_0$ |
|---|---|---|---|---|---|---|---|
| 2 0 0 | v.s. | 4 0 2 | v.s. | 0 1 7 | v.s. | 1 2 0 | s. |
| 4 0 0 | v.s. | $\bar{4}$ 0 2 | v.w. | 0 1 8 | v.s. | 1 4 0 | v.s. |
| 6 0 0 | w. | $\bar{4}$ 0 4 | w. | 0 2 1 | v.v.w. | 1 6 0 | v.s. |
| 0 2 0 | v.w. | 4 0 6 | v.s. | 0 2 2 | v.v.w. | 1 1 1 | v.v.w. |
| 0 4 0 | s. | 5 0 1 | v.w. | 0 2 4 | v.v.w. | 1 1 3 | w. |
| 0 6 0 | s. | $\bar{5}$ 0 1 | v.s. | 0 2 5 | v.s. | 1 1 5 | w. |
| 0 8 0 | s. | | | 0 2 6 | v.s. | 1 1 6 | w. |
| 0 0 $\bar{2}$ | s. | 5 0 3 | m.s. | 0 2 7 | v.s. | 1 1 7 | m.s. |
| 0 0 4 | v.s. | $\bar{5}$ 0 3 | w. | 0 4 1 | m.s. | 1 2 1 | v.w. |
| 0 0 6 | v.s. | 5 0 5 | w. | 0 4 2 | v.v.w. | 1 2 4 | w. |
| 0 0 8 | s. | 5 0 7 | m.s. | 0 4 4 | v.v.w. | 1 2 5 | v.v.w. |
| 1 0 1 | w. | | | 0 4 5 | s. | 1 2 7 | v.v.w. |
| $\bar{1}$ 0 1 | m.s. | 6 0 2 | v.s. | 0 4 6 | v.s. | 1 2 8 | m.s. |
| 1 0 3 | m.s. | 6 0 4 | w. | 0 4 7 | s. | 1 3 2 | s. |
| $\bar{1}$ 0 3 | s. | 6 0 6 | v.s. | 0 5 1 | m.s. | 1 3 6 | w. |
| 1 0 5 | w. | 7 0 1 | m.s. | 0 5 3 | m.s. | 1 3 8 | m.s. |
| 1 0 7 | m.s. | 7 0 3 | m.s. | 0 5 5 | w. | 1 4 1 | w. |
| $\bar{1}$ 0 7 | v.s. | $\bar{7}$ 0 3 | m.s. | 0 5 7 | v.s. | 1 4 3 | w. |
| 2 0 2 | s. | | | 0 6 1 | s. | 1 4 5 | w. |
| $\bar{2}$ 0 2 | s. | 7 0 5 | v.s. | 0 6 2 | w. | 1 4 7 | w. |
| 2 0 4 | m.s. | $\bar{7}$ 0 5 | v.s. | 0 6 3 | v.w. | 1 4 8 | m.s. |
| $\bar{2}$ 0 4 | s. | $\bar{7}$ 0 7 | w. | 0 6 4 | m.s. | 1 5 2 | s. |
| 2 0 6 | v.s. | $\bar{7}$ 0 9 | v.s. | 0 6 5 | v.s. | 1 5 5 | m.s. |
| 3 0 1 | m.s. | 8 0 2 | v.s. | 0 6 6 | v.s. | 1 5 7 | m.s. |
| $\bar{3}$ 0 1 | v.s. | 8 0 4 | v.s. | 0 7 2 | s. | 1 6 2 | w. |
| 3 0 3 | m.s. | 0 1 3 | s. | 0 7 3 | m.s. | 1 6 5 | s. |
| $\bar{3}$ 0 3 | v.s. | 0 1 4 | m.s. | 0 7 4 | v.s. | 1 7 1 | m.s. |
| 3 0 5 | w. | | | | | 1 7 2 | s. |
| $\bar{3}$ 0 5 | v.s. | 0 1 5 | v.v.w. | | | 1 7 5 | w. |
| 3 0 7 | w. | 0 1 6 | w. | | | 1 8 1 | m.s. |

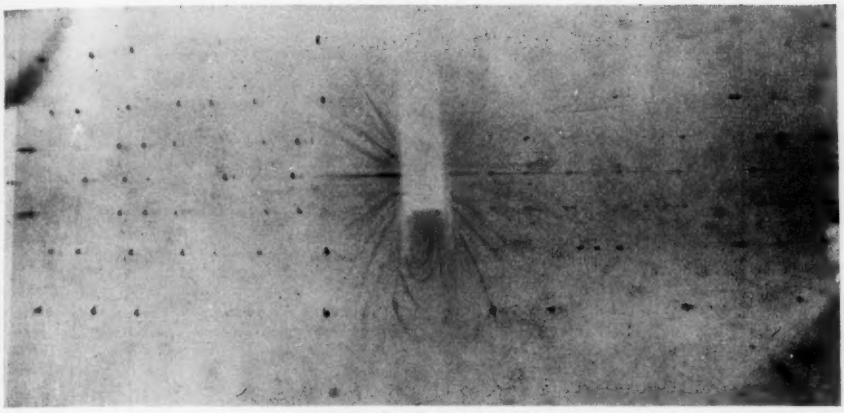

FIG. 1 (Oscillation *b*-axis).

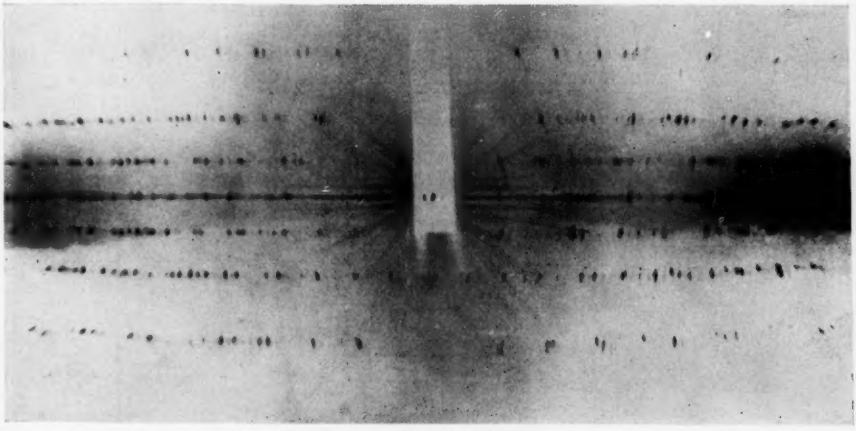

FIG. 2 (Rotation *a*-axis).

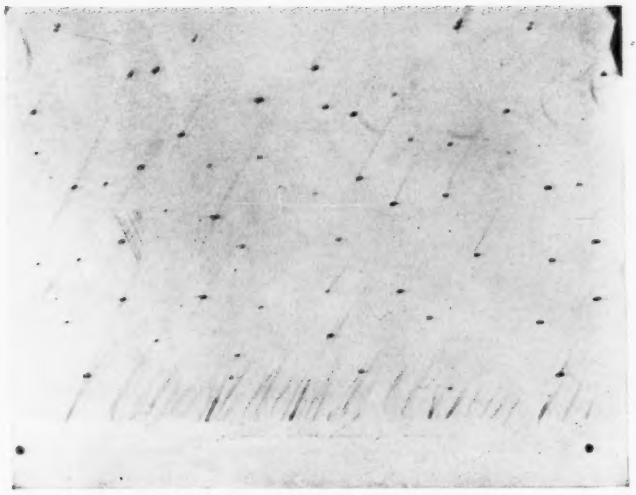

FIG. 3 (Weissenberg *b*-axis zero layer).

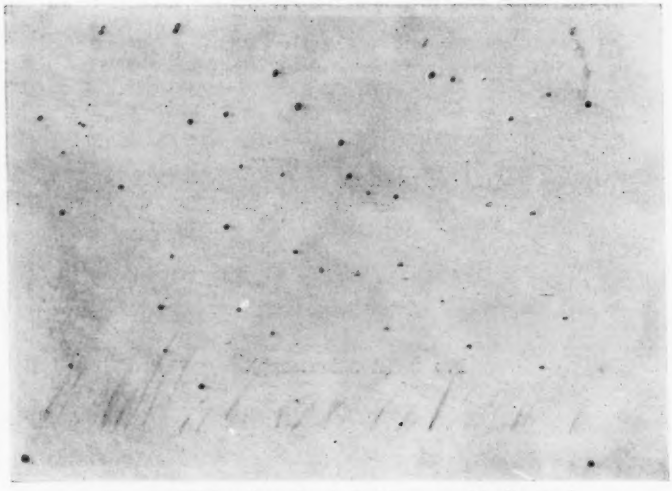

FIG. 4 (Weissenberg *b*-axis first layer equi-inclination).

The rotation photographs show the layer lines quite clearly indicating that the piece used was a single crystal and that the setting was accurate. This is further supported by the perfect Weissenberg pictures from which the $c$-axis and angle $\beta$ were calculated. In fact these represent the first published single crystal photographs of thorium-bearing monazite.

It would be seen that ($h$ $o$ $l$) planes are halved when $(h + l)$ is odd and ($o$ $k$ $o$) planes are halved when $k$ is odd. The space group is thus $P2_{1/n}$ ($C^5_{2h}$).

## Summary

Rotation and Weissenberg pictures have been taken of thorium-bearing monazite single crystal. The cell parameters are $a_0 = 6{\cdot}66$ Å, $b_0 = 6{\cdot}98$ Å, $c_0 = 6{\cdot}32$ Å and $\beta = 76°\ 38'$. The space group determined is $P2_{1/n}$ ($C^5_{2h}$).

## Bibliography

1. Karkhanavala and Shankar .. *Proc. Ind. Acad. Sci.*, 1954, **60 A** (2), 67.
2. Ramdohr Klochmann .. *Lehrbuch der Mineralogie Stuttgart*, 1936.
3. Gliszczynski, S. V. .. *Zeit. Krist*, 1939, **101**, 1.
4. Pabst, A. .. *Amer. Mineral*, 1951, **36**, 60.

# POLAROGRAPHIC INVESTIGATION OF CADMIUM FERROCYANIDE COMPLEX

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Received July 2, 1956

(Communicated by S. N. Gundu Rao, F.A.SC.)

## Introduction

The formation of complex(es) of cadmium and ferrocyanide has attracted much attention in recent years. Tananaev and Kozlov[1] studied the dependence of the composition of the complexes formed on the concentration of the reacting substances. From direct volumetric titrations, using 3:3′ dimethylnaphthidine, napthidine and O-dianisidine as indicators, Belcher *et al.*[2] observed that the white precipitate formed by the interaction of $Cd^{++}$ and $[Fe\ (CN)_6]^{-4}$ was of the composition $Cd_5K_6\ [Fe\ (CN)_6]_4$. Using phenanthroline ferrous complex as the indicator, Deshmukh and Venugopalan[3] found that the composition of the precipitate was $CdK_2Fe\ (CN)_6$ or $Cd_5K_6\ [Fe\ (CN)_6]_4$ according as the concentration of 1% or 2–4% of ferrocyanide solution used. The present communication reports the investigation of composition of the cadmium ferrocyanide complex by polarographic method, which required the use of none of the indicators employed by other workers.

## Experimental

The cadmium sulphate used was B.D.H. Analar sample; this was purified by recrystallisation in twice distilled water and dried at 160° C. in a dust-free chamber. A stock solution of $CdSO_4$ was prepared by dissolving a known quantity of the purified sample in water. The strength of this solution was estimated gravimetrically as pyridine thiocyanate.[4]

The potassium ferrocyanide used was Merck sample.

KCl, $NH_4Cl$, KBr, $KNO_3$, $K_2SO_4$ and $(NH_4)_2SO_4$ used (as supporting electrolytes in the polarographic technique, *vide infra*) were all Merck samples.

The polarograph employed was assembled in this Laboratory, and was described in an earlier communication.[5] The following were the characteristics of the capillary employed:

Time $t$ for one drop $= 2 \cdot 5$ sec. (in 0·1 N KCl).

Mass $m$ of a drop $= 0{\cdot}78$ mgm.

The polarographic method of investigation of the cadmium ferrocyanide complex involved the execution of amperometric titration of a known volume of cadmium solution against standard $K_4Fe(CN)_6$. For this purpose 25 ml. of the cadmium solution were taken in a cell containing mercury which served as the pool electrode in the polarographic technique; the other electrode, *viz.*, dropping mercury electrode was made as the cathode. The titrations were carried out at $-0{\cdot}9$ volt *vs.* S.C.E. where the diffusion current in the cathodic reduction wave of $Cd^{++}$ attained a limiting value which was proportional to the concentration of $Cd^{++}$.[5] The investigations were made with different supporting electrolytes listed above. No gelatine solution has been added since $Cd^{++}$ does not exhibit any polarographic maximum.

## Results and Discussions

Fig. 1 gives a typical group of results on the variation of the diffusion current of $Cd^{++}$ at $-0{\cdot}9$ volt *vs.* S.C.E., during the titration against $K_4Fe(CN)_6$. In this, curves 1, 2 and 3 refer respectively to the experiments

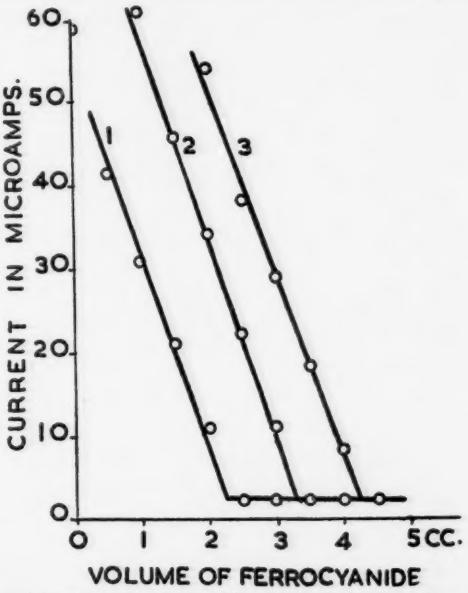


Fig. 1. Amperometric titration of Cadmium with Potassium Ferrocyanide.

Concentration of $Cd^{++} = 12$ mM; Concn. of $K_4Fe(CN)_6 = 100$ mM. Curve 1 refers to supporting electrolyte KCl; 2 to KBr and 3 to $KNO_3$, of 0·5 M. The scale on the abscissa refers to curve 1; and the curves 2 and 3 have been progressively shifted by 1 c.c.

in which KCl, KBr and $KNO_3$ were used as the supporting electrolytes. On addition of $K_4Fe(CN)_6$ the diffusion current decreased progressively in proportion to the decrease in the concentration of $Cd^{++}$. The current diminished during titration till it became, at the end point, very small, equal to the residual current of the medium. Further addition of $K_4Fe(CN)_6$ did not produce any change in the current in accord with the finding that $K_4Fe(CN)_6$ was not reduced at the dropping mercury electrode.[6] Similar results were obtained with other supporting electrolytes. It may be added that the use of KCl, KBr, etc., not only served as the supporting electrolytes necessary in the polarographic investigation but also made the precipitated complex to settle rapidly.

Table I gives the titre values obtained with different supporting electrolytes. In this, the data in column 3 give the actual volume of $K_4Fe(CN)_6$

TABLE I

*Amperometric Titration of Cadmium*

| Strength of Cd solution in mM | Strength of $K_4Fe(CN)_6$ solution in mM | Volume of $K_4Fe(CN)_6$ actually required in ml. | Volume of $K_4Fe(CN)_6$ solution in ml. calculated according to the formula | |
|---|---|---|---|---|
| | | | $CdK_2Fe(CN)_6$ | $Cd_5K_6[Fe(CN)_6]_4$ |
| (1) | (2) | (3) | (4) | (5) |
| | | (*a*) *Supporting electrolyte* = 0·5 *M KCl* | | |
| 12 | 100 | 2·45 | 3·0 | 2·4 |
| 10 | 100 | 2·00 | 2·5 | 2·0 |
| 12 | 50 | 4·80 | 6·0 | 4·8 |
| 10 | 50 | 4·05 | 5·0 | 4·0 |
| 8 | 50 | 3·20 | 4·0 | 3·2 |
| 6 | 50 | 2·45 | 3·0 | 2·4 |
| 12 | 25 | 9·60 | 12·0 | 9·6 |
| 10 | 25 | 8·00 | 10·0 | 8·0 |
| 8 | 25 | 6·40 | 8·0 | 6·4 |
| 6 | 25 | 4·75 | 6·0 | 4·8 |
| | | (*b*) *Supporting electrolyte* = 0·5 *M KBr* | | |
| 15 | 100 | 3·05 | 3·75 | 3·0 |
| 12 | 100 | 2·45 | 3·0 | 2·4 |
| 12 | 50 | 4·80 | 6·0 | 4·8 |
| 10 | 50 | 4·05 | 5·0 | 4·0 |
| 10 | 25 | 7·95 | 10·0 | 8·0 |
| 8 | 50 | 3·25 | 4·0 | 3·2 |
| 8 | 25 | 6·40 | 8·0 | 6·4 |
| 6 | 25 | 4·80 | 6·0 | 4·8 |

TABLE I—*Contd.*

| Strength of Cd solution in mM | Strength of $K_4Fe(CN)_6$ solution in mM | Volume of $K_4Fe(CN)_6$ actually required in ml. | Volume of $K_4Fe(CN)_6$ solution in ml. calculated according to the formula | |
|---|---|---|---|---|
| | | | $CdK_2Fe(CN)_6$ | $Cd_5K_6[Fe(CN)_6]_4$ |
| (1) | (2) | (3) | (4) | (5) |
| | | (*c*) *Supporting electrolyte* = 0·5 *M* $KNO_3$ | | |
| 15 | 100 | 3·00 | 3·75 | 3·0 |
| 12 | 100 | 2·40 | 3·0 | 2·4 |
| 12 | 50 | 4·75 | 6·0 | 4·8 |
| 10 | 50 | 4·00 | 5·0 | 4·0 |
| 8 | 50 | 3·20 | 4·0 | 3·2 |
| 12 | 25 | 9·60 | 12·0 | 9·6 |
| 10 | 25 | 8·00 | 10·0 | 8·0 |
| 8 | 25 | 6·40 | 8·0 | 6·4 |
| | | (*d*) *Supporting electrolyte* = 0·25 *M* $K_2SO_4$ | | |
| 15 | 100 | 3·00 | 3·75 | 3·0 |
| 12 | 100 | 2·40 | 3·0 | 2·4 |
| 10 | 50 | 3·70 | 5·0 | 4·0 |
| 8 | 50 | 3·00 | 4·0 | 3·2 |
| 8 | 25 | 6·10 | 8·0 | 6·4 |
| 6 | 25 | 4·50 | 6·0 | 4·8 |
| | | (*e*) *Supporting electrolyte* = 0·5 *M* $(NH_4)_2SO_4$ | | |
| 12 | 100 | 2·35 | 3·0 | 2·4 |
| 12 | 50 | 4·50 | 6·0 | 4·8 |
| 10 | 50 | 3·80 | 5·0 | 4·0 |
| 8 | 50 | 3·30 | 4·0 | 3·2 |
| 6 | 50 | 2·40 | 3·0 | 2·4 |
| 12 | 25 | 8·70 | 12·0 | 9·6 |
| 10 | 25 | 7·40 | 10·0 | 8·0 |
| 8 | 25 | 6·00 | 8·0 | 6·4 |
| | | (*f*) *Supporting electrolyte* = 0·5 *M* $NH_4Cl$ | | |
| 15 | 100 | 3·00 | 3·75 | 3·0 |
| 12 | 100 | 2·45 | 3·0 | 2·4 |
| 12 | 50 | 4·80 | 6·0 | 4·8 |
| 8 | 50 | 3·25 | 4·0 | 3·2 |
| 10 | 25 | 8·00 | 10·0 | 8·0 |
| 8 | 25 | 6·45 | 8·0 | 6·4 |

required for 25 ml. of $Cd^{++}$ solution of known strength while those in columns 4 and 5 refer to the same calculated on the basis that the complex formed according to the following equations:

$$CdSO_4 + K_4Fe(CN)_6 \rightarrow CdK_2Fe(CN)_6 + K_2SO_4 \quad \text{(i)}$$

$$5\,CdSO_4 + 4\,K_4Fe(CN)_6 \rightarrow Cd_5K_6[Fe(CN)_6]_4 + 5\,K_2SO_4 \quad \text{(ii)}$$

It was instructive to note that over the entire range of concentrations of $K_4Fe(CN)_6$ and of $CdSO_4$ studied, the observed titre values (column 3) agreed closely with those calculated (column 5, Table I) from eq. (ii). It appeared, therefore, that the composition of the precipitated complex was $Cd_5K_6[Fe(CN)_6]_4$.

It may be added that the present studies indicate a simple method for quantitative estimation of $Cd^{++}$ using $K_4Fe(CN)_6$. The data in Table I show that the error involved in the analysis is about 1 per cent.

## SUMMARY

The composition of cadmium ferrocyanide complex was investigated polarographically using KCl, KBr, $KNO_3$, $(NH_4)_2SO_4$, $K_2SO_4$ and $NH_4Cl$ as the supporting electrolytes. Amperometric titrations indicated that the composition of precipitated complex was $Cd_5K_6[Fe(CN)_6]_4$. The results showed the possibility of amperometric estimation of $Cd^{++}$ by $Fe(CN)_6^{-4}$ within an error 1 per cent.

## ACKNOWLEDGEMENT

Authors' thanks are due to Professor S. N. Gundu Rao, B.SC., A.H.B.T.I., F.R.I.C., F.A.SC., Director, Indian Institute of Sugar Technology, Kanpur, for his keen interest in the work, and to the Ministry of Education, Government of India, for a Fellowship to one of us (S.K.D.A.).

## REFERENCES

1. Tananaev, V. T. and Kazlov, A. S. — *Zhur. Anal. Chim.*, 1951, **6**, 149.
2. Belcher, R., Nutten, A. J. and Stephen, W. I. — *J. Chem. Soc.*, 1951, 3444.
3. Deshmukh, G. S. and Venugopalan, M. — *J. Ind. Chem. Soc.*, 1956, **33**, 222.
4. Vogel, A. I. .. *Text Book of Inorganic Analysis*, 1951, p. 428. Longmans.
5. Ramaiah, N. A. and Agarwal, S. K. D. — *Proc. Ind. Acad. Sci.*, 1956, **44A**, 26.
6. Sanigar, G. .. *Trav. Chim. Pays. Bas.*, 1925, **44**, 59.

# A STUDY OF THALLOUS-THIOCYANATE SYSTEM

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Received July 28, 1956

(Communicated by Dr. H. J. Bhabha, F.R.S., F.A.Sc.)

## Introduction

This paper presents the results of a polarographic investigation of thallous thallium in potassium thiocyanate where the half-wave potential, diffusion coefficient, etc., have been determined and of the determination of the activity coefficients of thallous thiocyanate in potassium thiocyanate from solubility measurements.

## Experimental

*Reagents.*—A stock solution of standard thallium nitrate was prepared from weighed amounts of E. Merck C.P. salt.

Thallous thiocyanate was prepared from thallous nitrate and B.D.H. AR potassium thiocyanate. The precipitate was washed well, dried at 110° C. and bottled.

A stock solution of 1·5 M potassium thiocyanate was prepared from B.D.H. AR salt and standardised by Volhard's method.[1] The solutions used were obtained by appropriate dilution of this stock solution.

## Results and Discussion

*Polarographic Study of Thallium in Potassium Thiocyanate.*—Data for polarograms were obtained on a manual polarograph.[2] The potential applied at the electrode terminals and the current calculated in terms of the *i*R drop across a 10,000 ohms resistance were measured with a Leeds Northrup students' potentiometer using a Cambridge spot galvanometer as a null instrument. An H-type cell[3] was used in which a saturated calomel electrode served as a reference electrode. Thymol ($2\times10^{-4}$ per cent.) was used as a maximum suppressor. All measurements were made at $30{\cdot}0 \pm 0{\cdot}1°$ C. In all cases oxygen was removed by passing nitrogen through the solution for about 15 minutes.

The solubility of thallium in 0·1 M potassium thiocyanate was found from solubility measurements to be about 5 mM showing that this would be a suitable medium to study. The plot of $E_{d.e}$ *vs.* log $i/i_d$-$i$ in 0·1 M

thiocyanate gave a straight line having a slope of 0·061 V. Thus the number of electrons involved in the electrode reaction is one. The intercept on the X-axis led to a value of $-0{\cdot}470 \pm 0{\cdot}005$ V for the half-wave potential, its value in a non-complexing electrolyte such as 0·1 M potassium chloride being $-0{\cdot}460$ V.[4] It was observed that the half-wave potential remained unaffected with the change of concentration of thiocyanate (0·1 to 0·5 M); thus the reduction of thallium in this medium was that of a simple metal ion.

A diffusion current constant was calculated using the equations of Lingane[5] and Lingane and Loveridge[6] and the values were found to be 2·85 and 2·43 respectively. The value of the capillary constant $m^{2/3}t^{1/6}$ was determined as 2·03 mg.$^{2/3}$sec.$^{-1/2}$ at $-0{\cdot}8$ V *vs.* s.c.e. At $-0{\cdot}8$ V the diffusion current-concentration ratio was $5{\cdot}80 \pm 0{\cdot}05\,\mu$A per mM per litre between 0·25 and 2·0 mM thallium.

The diffusion coefficient for the thallous ion calculated from Ilkovic's equation[7] worked out as $2{\cdot}21 \times 10^{-5}$ cm.$^2$sec.$^{-1}$ which agreed well with the value $2{\cdot}00 \times 10^{-5}$ cm.$^2$sec.$^{-1}$ obtained from conductivity data.[8]

*Studies on the Solubility of Thallous Thiocyanate.*—The solubility of thallous thiocyanate in different concentrations of potassium thiocyanate was measured. The salt in sufficient excess was mechanically agitated with the solution in a 250 ml. pyrex bottle kept in a water-bath at $30{\cdot}0 \pm 0{\cdot}1°$ C. till equilibrium was attained. The solution was filtered through Whatman No. 42 paper and thallium estimated by the chromate method.[9]

The polarographic investigation had revealed the absence of any complex formation between thallous ions and thiocyanate ions. This was confirmed since a plot of the concentration of thiocyanate against solubility of thallium did not indicate any minima.[10]

The solubility data were further used to calculate the activity coefficients and activity solubility product of thallous thiocyanate in potassium thiocyanate at 30° C.[11] The mean ionic molality $m_\pm$ of thallous thiocyanate calculated from the solubilities in presence of different concentrations of potassium thiocyanate was plotted against the square root of ionic strength (Fig. 1). A straight line was obtained which gave on extrapolation to infinite dilution the value of $K_s^{1/2}$ equivalent to $15{\cdot}25 \times 10^{-3}$. The activity coefficient $r_\pm$ of thallous thiocyanate was then calculated from the equation:

$$r_\pm = \frac{K_s^{\frac{1}{2}}}{m_\pm}$$

where $K_s$ is the activity solubility product. The results are tabulated in Table I. The activity solubility product of thallous thiocyanate at 30° C. is $23{\cdot}1 \times 10^{-5}$.

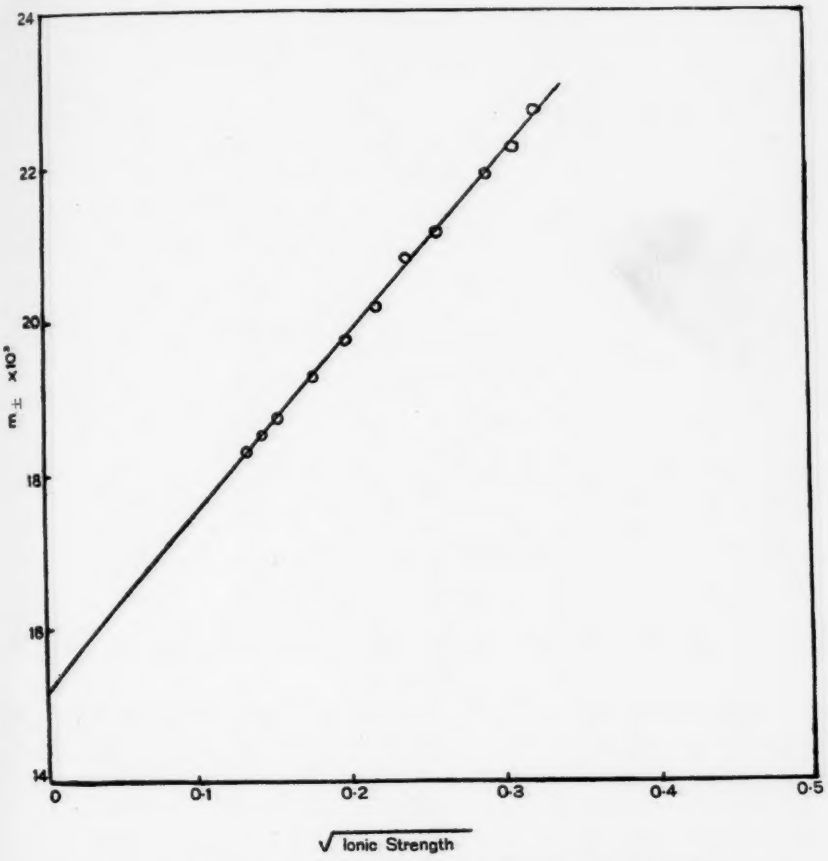


FIG. 1. Solubility of Thallous Thiocyanate in Potassium Thiocyanate. Plot of Mean Ionic Molality *vs.* The Square Root of the Ionic Strength.

TABLE I

*Activity Coefficients of Thallous-Thiocyanate in Potassium Thiocyanate at 30° C.*

| Concentration of potassium thiocyanate in M | Activity Coefficient |
|---|---|
| 0·0 | 0·825 |
| 0·005 | 0·815 |
| 0·01 | 0·805 |
| 0·02 | 0·784 |
| 0·03 | 0·765 |
| 0·04 | 0·749 |
| 0·05 | 0·727 |
| 0·06 | 0·703 |
| 0·08 | 0·690 |
| 0·09 | 0·679 |
| 0·10 | 0·666 |

SUMMARY

The reduction of thallium in thiocyanate involves a one-electron reduction. In 0·1 M KCNS, the $E_{\frac{1}{4}}$ is $-0{\cdot}470$ V *vs.* s.c.e. The diffusion coefficient and the diffusion current constant are determined. As the $E_{\frac{1}{4}}$ does not change with the concentration of thiocyanate the reduction is that of a simple metal ion. The activity coefficient for thallous thiocyanate in potassium thiocyanate and the activity solubility product are calculated from solubility measurements.

REFERENCES

1. Scott .. *Standard Methods of Chemical Analysis*, 5th Ed., **1**, D. Van Nostrand Co., Inc., 824.
2. Kolthoff, I. M. and Lingane, J. J. *Polarography*, **1**, Interscience Publishers, N.Y., 1952, 297.
3. ———— .. *Ibid.*, p. 354.

4. Lingane, J. J. .. *J.A.C.S.*, 1939, **61**, 2099.
5. ———— .. *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 583.
6. —— and Loveridge, B. A. *J.A.C.S.*, 1950, **72**, 438.
7. Ilkovic, D. .. *Coll. Czec. Chem. Communs.*, 1934, **6**, 498.
8. Kolthoff, I. M. and Lingane, J. J. *Polarography*, Interscience Publishers, N.Y., 1952, **1**, 52.
9. Scott .. *Standard Methods of Chemical Analysis*, 5th Ed., **1**, 944. D. Van Nostrand Co. Inc.
10. Reynolds, C. A. and Argersinger Jr., W. T. *J. Phys. Chem.*, 1952, **56**, 417.
11. Glasstone, D. .. *Thermodynamics for Chemists*, 5th Ed., 1950, p. 398. D. Van Nostrand Co., Inc.

# DETERMINATION OF URANIUM CONTENT IN RADIOACTIVE MINERALS BY AUTORADIOGRAPHY

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Received July 28, 1956

(Communicated by Dr. H. J. Bhabha, F.R.S., F.A.SC.)

## Abstract

Nuclear track plates serve as a rapid and cheap tool in the identification and estimation of radioactive minerals in ore specimens, microsections and sand-grains. A method of estimation of the uranium content of the minerals from photographic density was studied.

This method avoids the tedious process of counting large number of tracks recorded in the nuclear emulsion by the radioactive minerals. The effects of (1) uranium content of the mineral specimens, (2) duration of exposure of the plate to the mineral specimens, (3) period of development of the plates and (4) temperature of the developer bath, on photographic density were studied.

## Introduction

Niepec de Saint Victor (1867), Henri Becquerel (1896), and Madame Curie (1898) had observed that both uranium and thorium compounds produced a developable image on photographic plates even when they were separated from the source by black paper. Campbell and Wood (1906) recorded that potassium compounds also activate the photographic plate. However, since the photographic emulsions used by the earlier workers could not differentiate between the various types of radiations, work could not progress in this direction till special types of emulsions were developed.

It was Reinganum (1911) who first observed that the blackening of the photographic emulsion, when caused by alpha particles, was due to an aggregate of alpha tracks, each formed by a row of silver grains in the developed emulsion. Since this discovery and since its potential uses in nuclear research was realised, special plates made by Kodak, and Ilford, Ltd., have come into the market. These special nuclear emulsion plates of variable thickness and composition are capable of recording alpha radiation, beta radiation and electrons liberated by gamma radiation either separately or together. The Ilford C-2 and the Kodak NT-1 *a* plates are specially designed to record only the heavy particles (mainly the alphas, protons and mesons)

but not the other radiations whereas the Ilford special lantern plates are so designed as to record primarily the beta radiations. The Ilford G-5 plates are sensitive to all charged particles.

For the identification of radioactive minerals in ores, alpha track emulsions are best suited in view of their relative insensitivity to visible light, beta radiations and electrons liberated by gamma radiations. They are sensitive primarily to protons, mesons and alpha particles. Alpha track plates give a more selective emission pattern and since the range of ionization of alpha radiations in these plates is of the order of 20 to 25 $\mu$, plates with a thickness of 50 $\mu$ are best suited for this type of work.

Alpha track plates supplied by Ilford, Ltd. (Ilford C2-50 $\mu$ plates), have been used throughout this work. The properties of these emulsions are recorded below (Yagoda, 1946).

*Elements in grams per c.c. of the emulsion*

| | | | |
|---|---|---|---|
| Ag | 1·87 | H | 0·056 |
| Br | 1·36 | O | 0·24 |
| I | 0·053 | N | 0·083 |
| C | 0·33 | S | 0·014 |

Traces of Ca, P, Cr, Si, Na

Grain diameter 0·16 $\mu$

## Experimental Procedure

In this investigation the effects of (1) uranium content of the mineral specimens, (2) duration of exposure of the plate to the active specimens, (3) period of development of the plates and (4) temperature of the developer bath, separately—on the photographic density (D) were studied keeping the other factors constant.

The minerals were cut into small pieces about one-half inch square and ¼″ thick. Only those pieces whose surfaces showed uniform distribution of activity were selected. These were polished with coarse carborundum, fine carborundum and microid alumina successively. Before transferring from one polishing disc to the next, the specimen was thoroughly washed to free it from any adhering abrasive. The polished chips were mounted in wax. The exposure was made in a special camera and the entire unit was stored in a light proof box kept in a desiccator.

Care was taken to see that the specimen was not displaced laterally relative to the nuclear plate once the contact was established since the

emulsion is particularly sensitive to directional (tangential) pressure. After the necessary exposure was made, the nuclear plate was removed and developed in Kodak D 19 for 4 minutes at 26° C., with intermittent agitation, unless otherwise specified. It was next washed in an acetic acid stop bath, and fixed in Kodak F-5 till the plate was clear. The remaining hypo was washed off in a continuous stream of water for 30 minutes and the plate dried in a dust-free atmosphere. The opacity of the blackening, produced by the specimen, was measured using a Mole Recording Microphotometer.

The instrument was so adjusted that the galvanometer deflection was 100 units when the clear plate was interposed in the path of the standard light, and 0 when the light was completely cut off. The adjustment was made for each plate separately in view of the different degrees of background fogging in them. From the amount of light transmitted in each case, the photographic density ' D ' was calculated using the formula

$$D = \log_{10} I_0/I_t \qquad I_0 = \text{Incident light}$$

$$I_t = \text{Transmitted light}$$

TABLE I

| No. of mineral | % $U_3O_8$ equiv.* | Period of exposure | $U_3O_8$ days (2×3) | % Transmitted light | Photographic density-D |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 1 | 12·17 | 7 days | 85·19 | 26 | 0·59 |
| 2 | 16·60 | 7 days | 116·20 | 21 | 0·68 |
| 3 | 38·40 | 1 day | 38·40 | 40 | 0·40 |
| 4 | 43·00 | 2 days | 86·00 | 25 | 0·60 |
| 5 | 43·00 | 1 day | 43·00 | 36 | 0·420 |
| 6 | 67·20 | 1 day | 67·20 | 30 | 0·52 |
| 7 | 86·5 | 1 day | 86·5 | 25 | 0·60 |

* Radiometric assay.

TABLE II

| S. No. | Period of development (at 26° C.) | % Transmitted light | Photographic density-D |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 1 | 1 minute | 51 | 0·290 |
| 2 | 3 minutes | 40 | 0·398 |
| 3 | 5 minutes | 4 | 1·398 |
| 4 | 7 minutes | 2 | 1·699 |

TABLE III

| S. No. | Temperature of developer* | % Transmitted light | Photographic density-D |
|---|---|---|---|
| 1 | 23° C. | 11·5 | 0·939 |
| 2 | 26° C. | 4·0 | 1·398 |
| 3 | 29° C. | 0·5 | 2·301 |
| 4 | 32° C. | 0 | .. |

* Period of Development—4 Minutes.

## RESULTS AND DISCUSSION

These results are shown in Figs. 1 and 2, where the X-axis represents the photographic density and the Y-axis, the second variable.

Graph 1 shows a straight line relationship between the product of $U_3O_8$ and exposure time (in days) against the photographic density.

The absolute value of the density depends upon the following factors:

(1) The type and age of the emulsion.

(2) Conditions of development producing variable development fog.

(3) The disintegration products of uranium in the mineral which may produce background fog since the emulsion is not completely insensitive to beta and gamma radiations.

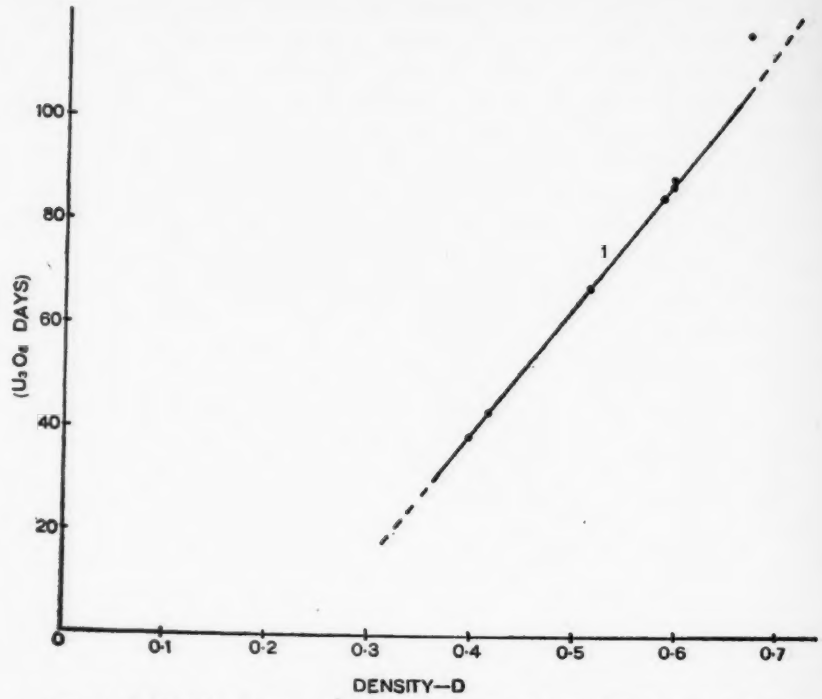


FIG. 1. Relationship between photographic density and product of $U_3O_8$ and exposure (in days)—(1),

(4) The pressure exerted by the specimen itself on the emulsion, which produces certain fogging under the specimen because of the sensitivity of the emulsion to strain, irrespective of the activity of the specimen.

Of the above factors the effect of the first three are on the entire plate while the fourth is on the exposed area only. The procedure adopted, namely adjusting the clear-plate reading in the microphotometer to 100, effectively eliminates the first three factors. In order to make the fourth factor constant, the exposure of the plate was made in a special camera with sponge cushions, and fixed pressure.

The slope of the graph is characteristic of the emulsion itself. Even though it can perhaps be changed slightly by the use of different developers, no attempt was made in these investigations to study it. For the estimation of the activity, only the straight line portion of the graph can be used.

If the same type of emulsion is used, the blackening produced is a measure of the $U_3O_8$ content of the mineral and its exposure period provided the processing conditions are kept constant. Since the exposure is a known quantity, the $U_3O_8$ content of the mineral can be easily obtained from the graph. It is also possible to estimate the amount of $U_3O_8$ and $ThO_2$ present in the same radioactive mineral by autoradiographic technique (Bowie, 1951). Standardization of this procedure is in progress.

Graph 2 shows that the photographic density reaches a maximum for a certain period of development and the rate of increase in density thereafter

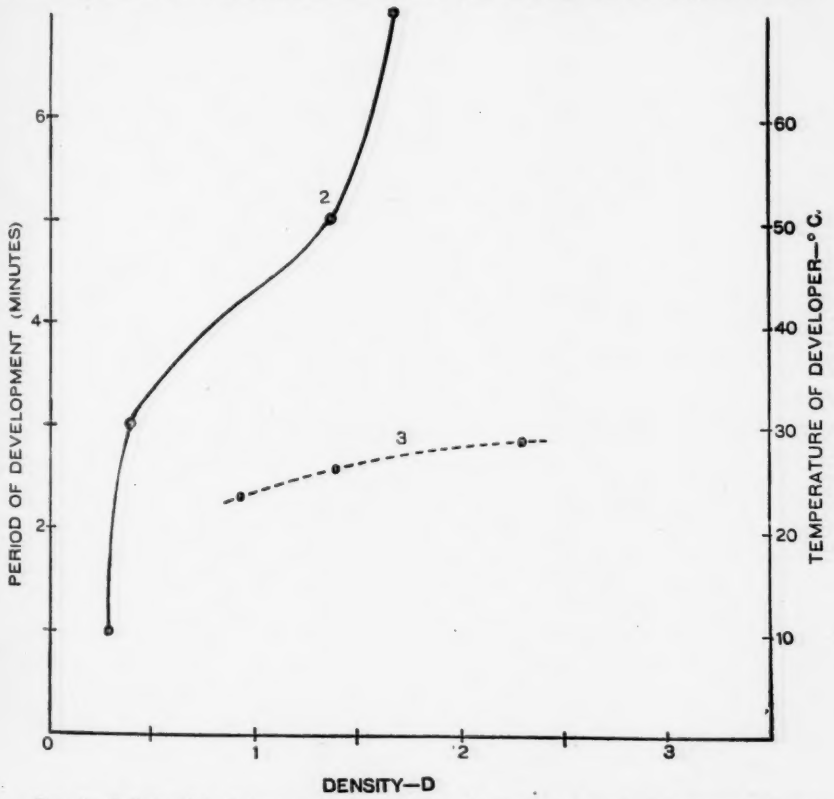


FIG. 2. Relationship between photographic density and period of development (2), and Temperature of developer (3).

is negligible. The effect of temperature of developer bath on photographic density is more or less similar (Graph 3). Nuclear plates developed at 32° C. showed marked reticulation.

## CONCLUSIONS

Nuclear track plates serve as a rapid and cheap tool in the identification of and estimation of radioactive minerals in ores. The measurement of photographic density and determination of the uranium content of the mineral therefrom is very useful in that it avoids the tedious process of counting a few thousand alpha tracks. Besides, where the identification of the mineral is facilitated by the estimation of its $U_3O_8$ content and where the available specimen is either too small or is needed for further petrographic study, this method gives a fairly accurate estimate of its uranium content, without destroying the specimen.

The period of development at 26° C. might range from 3 to 5 minutes, using full strength developer. The change in the photographic density by slight increase or decrease in the period of development is small. It is advisable to keep the temperature of the processing baths at about 25°–29° C. The rate of development below this range is rather slow. At higher temperatures of the developer, reticulation and a high degree of fogging was observed in the emulsions.

Since the relationship between period of exposure and density is also linear over a wide range, considerable latitude exists in the selection of exposure period.

The applicability of this procedure in case of small grains of active minerals is being studied.

## REFERENCES


1. Niepec de Saint Victor — *Compt. Rend. Acad. Sci., Paris*, 1867, **60**, 505.
2. Becquerel, H. .. *Ibid.*, 1896, **122**, 420–501.
3. Curie, M. S. .. *Ibid.*, 1898, **126**, 1101.
4. Campbell, N. R. and Wood, A. — *Proc. Cambridge Phil. Soc.*, 1906, **14**, 15.
5. Reinganum .. *Physik. Zeit.*, 1911, **12**, 1076.
6. Tyler, S. A. and Marais, J. J. — *Journ. Sed. Petrology*, 1941, **11**, 145.
7. Goodman, Clark and Thomson, G. A. — *Amer. Min.*, 1943, **28**, 456.
8. Yagoda, H. .. *Ibid.*, 1946, **31**, 87 and 462.
9. Pelc, S. R. .. *Nature*, 1947, **160**, 749.
10. Berriman, R. W. .. *Ibid.*, 1948, **162**, 992.
11. Webb, J. H. .. *Phys. Review*, 1948, **74**, 511.
12. Yagoda, H. .. *Radioactive Measurements with Nuclear Emulsions*, 1949. John Wiley & Sons, New York.
13. Poole, J. H. J. and Bremner, J. W. — *Nature*, 1949, **163**, 130.

14. Berriman, R. W., Herz, R. H. and Stevens, G. W. W. — *Brit. Journ. Radiology*, 1950, **23**, 472.
15. Doniach, I. and Pelc, S. R. — *Ibid.*, 1950, **23**, 184.
16. Wiener, Martin and Yagoda, H. — *Rev. Sci. Instr.*, 1950, **21**, 39.
17. Bowie, S. H. U. .. *Bull. Geol. Soc. of Gt. Britain*, 1951, **3**, 58.
18. Ford, I. H. .. *Nature*, 1951, **167**, 273.
19. Brode, W. R. .. *Chemical Spectroscopy*, 1952. John Wiley & Sons, New York.
20. Robinson, S. C. .. *Amer. Min.*, 1952, **37**, 544.

1026–56 Printed at The Bangalore Press, Bangalore City, by C. Vasudeva Rao, Superintendent
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